

# **California State Water Resources Control Board**

## **Draft for Public Comment**

### **Leaking Underground Fuel Tank Guidance Manual**

**Version 1.0 – August 3, 2010**



California State Water Resources Control Board  
Leaking Underground Fuel Tank Guidance Manual

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# Overview of the California Leaking Underground Fuel Tank (LUFT) Manual



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## Intent of the California LUFT Manual

The intent of the California LUFT Manual (CA LUFT Manual, Manual) is to provide guidance to stakeholders and to assist them in making informed decisions regarding the investigation and cleanup of unauthorized releases of fuels from underground storage tanks (USTs) in the State of California. The Manual is designed to guide its users towards solutions for fuel-impacted sites; its contents are user-friendly and “state of the science.” This is the first revision of the Manual since October 1989. This revision reflects lessons learned and refinements in assessment and corrective action procedures.

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## Introduction

The CA LUFT Manual is intended to assist stakeholders involved in the California State Water Resources Control Board (SWRCB) LUFT Program to meet the Program’s main objective of protecting human health, safety, and the environment from petroleum products and/or petroleum additives which have leaked from USTs and/or their associated systems.

There are three primary sources where the legal requirements for investigation and cleanup of unauthorized releases from USTs are found:

- UST Regulations, California Code of Regulations (CCR) Title 23, Article 5 and Article 11
- State Board Policy 92-49, Policies and Procedures for the Cleanup and Abatement of Discharges under Water Code Section 13304
- California Health & Safety Code (H&SC) Sections 25280-25299.8, regarding public health and safety, and safety to the environment while dealing with underground tanks used for the storage of hazardous substances and wastes

**Definition.** An **unauthorized release**, as defined by H&SC Section 25295, is a release which escapes from the secondary containment, or from the primary containment, if no secondary containment exists, increases the hazard of fire or explosion, or causes any deterioration of the secondary containment of the underground tank system.

While these documents provide the legal requirements for performing investigation, cleanup, monitoring, and other activities at LUFT sites, they do not provide guidance on the best technical methods to perform these activities in the varied circumstances found at LUFT sites in the real world. This Manual provides information on “state of the science” technologies and implementation strategies that have been proven to be efficient and effective. Regulators, responsible parties (RPs), and consultants are encouraged to utilize this LUFT Manual to assist in the decision process of determining appropriate methods for compliance with regulations and policies at each individual site.

## Background

In mid-1985, the Department of Health Services (DHS) and the SWRCB formed a task force to establish procedures for determining whether a LUFT site was clean and safe, so as to protect public health and the environment. The procedures were contained in the 1989 *LUFT Field Manual*.

The statutory authority used to develop the *LUFT Field Manual* was the Porter-Cologne Water Quality Control Act, which called for the protection of water with the goal of removing “all” contamination from the soil, surface water, and groundwater affiliated with the site. However, the Task Force recognized “that this goal is unattainable at many sites. Typically, due to the lack of established scientific and technical knowledge, along with limited resources available to the property owner and local, state, and federal government agencies, most cleanup actions cannot achieve a zero contamination level” (State of California 1989).

Because the Task Force recognized that corrective actions would likely yield some level of residual contamination, it developed the following assumptions:

- 1) “Cleanup of all contaminated soil and dissolved product in groundwater is not always necessary to protect public health and the environment. However, it is desirable to clean up soils and groundwater to the maximum extent practical to reduce any future risk.

- 2) "All free product floating on groundwater should be removed, unless neither threat to beneficial uses of water nor danger to residents/workers from fire or explosion exists.
- 3) "Statewide cleanup levels for contaminated soil and dissolved product are undesirable. Because conditions vary from region to region, the task force decided to develop a general approach that can be used to quickly establish site-specific levels instead of setting state-wide cleanup levels."

The 1989 *LUFT Field Manual* was intended to provide guidance on the following:

- 1) Investigating suspected or known leaks at LUFT sites.
- 2) Assessing risk to human health and the environment when leaks have occurred.
- 3) Determining cleanup levels in soil, groundwater, and air for contaminated sites.
- 4) Screening out sites which represent an acceptable degree of risk from further study.
- 5) Taking remedial actions.

The original *LUFT Field Manual* was intended to avoid unwarranted analysis, while ensuring that adequate analysis was performed to identify the extent of contamination problems and more than 20 years later, this LUFT Manual has the same intentions.

## Scope of the CA LUFT Manual

Much experience, research, and gained knowledge has been incorporated into the UST Cleanup Program since the development of the 1989 *LUFT Field Manual*; however, the belief that removal of all contamination is unrealistic is still prevalent. The assumptions that were developed by the LUFT Task Force in 1989 are still applicable in 2010, specifically:

- 1) Cleanup of all contaminated soil and dissolved product in groundwater is not always necessary to protect human health, safety, and the environment.
- 2) Free product floating on groundwater should be removed, unless neither threat to beneficial uses of water nor danger to residents and workers from fire or explosion exists.

This Manual also has very similar goals to the 1989 Manual, including: providing guidance on investigating LUFT sites, assessing the risk of an unauthorized release, screening out sites which represent an acceptable degree of risk, and employing corrective actions. However, *unlike* the 1989 Manual, this Manual does not intend to determine cleanup levels for soil, groundwater, and air.

This Manual is intended for use as a guide for investigation and/or remediation of petroleum and fuel additive contaminants at LUFT sites which currently or potentially may impact human health, safety, and/or the environment. This Manual is **not intended** for use in the investigation or remediation of contaminants other than petroleum and fuel additives.

The Manual is a guidance document; it is not meant to supersede existing regulations regarding cleanup levels, regulatory processes, or other directives, but instead is intended to work in cooperation with such regulations.

Due to the diverse nature of the geology and hydrogeology throughout California, this LUFT Manual is designed to serve as a general resource document for the State of California. It does not include information specific to any county or region.

## Development of the CA LUFT Manual

The original 1989 *LUFT Field Manual* was the result of the best collective efforts put forth by local, regional, and state representatives. This Manual was also a collaborative effort but, in addition to local, regional, and state representatives, it has included input from the United States Environmental Protection Agency (USEPA) Region 9, RPs, consultants, and the general public. It was important for the SWRCB to give stakeholders an opportunity to play a role in the development of this Manual.

The process began with SWRCB hosting four public meetings across the state to collect information and ideas for updating the 1989 *LUFT Field Manual* and to invite discussion on how to improve the overall process of UST investigation and remediation within the state.

Raw input received at each of the four public meetings was consolidated into major topic areas, a Table of Contents was developed, and a wiki site was created to enable interested persons to contribute to the content of the Manual. The wiki site was open for five months, and much information was contributed from stakeholders across California.

Upon closure of the wiki site, Working Groups composed of regulators, consultants, and RPs formed to further refine specific chapters. The Working Groups reviewed the information that had been contributed by the public, filled in details where necessary, and distilled redundant information.

## **Content of the CA LUFT Manual**

The Manual is separated into three different sections: (1) Administration, (2) Initial Response, Reporting, and Tank Removal, and (3) LUFT Investigation and Remediation. The Manual is written and organized in a manner that encourages stakeholders to access the relevant information for which they are looking rather than read the Manual cover to cover.

### **Section 1: Administration**

This section of the Manual includes information on the maintenance, performance, organization, and management of the LUFT Program. It includes information such as the roles and responsibilities of parties, a summary of the UST Cleanup Fund (Fund), how to use the State's GeoTracker database, and provides guidance on properly developing work plans and reports.

### **Section 2: Initial Response, Reporting, and Tank Removal**

This section discusses the types of responses needed at LUFT sites based on the threat to human health, safety, and the environment. It also discusses initial reporting and abatement procedures, and proper tank removal.

### **Section 3: LUFT Investigation and Remediation**

This section discusses the fate and transport of petroleum in the subsurface, the crucial process of conceptualizing a LUFT site to make decisions, the investigation of soil, water, and soil vapor, and remedial actions.

## **References**

State of California. 1989. Leaking Underground Fuel Tank (LUFT) Task Force. *LUFT Field Manual*. Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. October.

# **CALIFORNIA LUFT MANUAL**

## **SECTION 1: ADMINISTRATION**

# Roles and Responsibilities

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## Scope of This Chapter

This chapter describes the roles and responsibilities of parties involved in LUFT sites throughout the State of California.

There are three primary parties involved in the investigation and remediation of LUFT sites: the responsible party (RP), the RP's authorized agent or consultant, and the lead regulatory agency overseeing the case. Each party has different roles and responsibilities, as discussed in subsequent sections of this chapter. This chapter provides information on the chief roles and responsibilities of each primary party, but **does not list** all possible roles and responsibilities.

Other stakeholders who may be involved in LUFT sites are adjacent property owners, the UST Cleanup Fund, the community, real-estate developers, etc.

## Responsible Party

California Health & Safety Code (H&SC), Sections 25280-25299.8 (regarding hazardous substances and waste stored in underground locations) and the California Code of Regulations (CCR), Title 23, Division 3, Chapter 16, "Underground Storage Tank Regulations," refer to the RP as "owner" and/or "operator."

"Owner" is defined in the California H&SC as "the owner of an underground storage tank" and "Operator" is defined as "any person in control of, or having daily responsibility for, the daily operation of an underground storage tank."

In the following sections, "RP" will be used interchangeably with "owner" and "operator."

The RP is responsible for complying with California H&SC Sections 25280-25299.8 and Articles 5 and 11 of the CCR "Underground Storage Tank Regulations." The RP's chief legal responsibilities are to comply with the California H&SC and Articles 5 and 11 of the CCR:

- Take corrective action in response to any unauthorized release, which may include preliminary site assessment and investigation.
- Report any unauthorized release from a UST or any spill or overfill to the regulatory agency if the RP or RP's agent is unable to clean up, or if the release, spill, or overfill is still under investigation within eight (8) hours of detection, as discussed in the [Initial Reporting and Abatement](#) chapter of this Manual.
- Notify the regulatory agency within 24 hours after an unauthorized release or condition has been detected and investigate the condition; take immediate measures to stop the release, and notify the State Office of Emergency Services.
- Submit a full written report within five working days of an unauthorized release. This report is to include pertinent information such as: RP and consultant name(s) and telephone number(s); list of type, quantities, and concentrations of hazardous substances released; the approximate date of release; etc. For further information regarding the information to be included, review CCR "UST Regulations," Section 2652.
- Notify the local HazMat agencies, fire departments, etc. when emergency/urgent response is needed at the site.
- Submit compliance reports, including soil and water chemistry analytical data and well data, to GeoTracker. The primary electronic reporting responsibilities for RPs are further discussed in the [GeoTracker](#) chapter of this Manual.
- Notify all impacted property owners of the proposed CAP and proposed closure.

The State of California retains the right to enforce penalties against the RP(s) if action is not taken or if the nature of the release is severe enough to warrant such action. Funding for clean-up activities may be available through the California Underground Storage Tank Cleanup Fund (Fund) for selected LUFT sites via reimbursement of submitted invoices. The [UST Cleanup Fund](#) chapter describes this process in greater detail.

State laws outline a regulatory structure that allows an RP to conduct the necessary site investigation and perform corrective actions in a timely and cost-effective manner.

RPs often contract with third-party environmental consultants to assist in the investigation and evaluation of a LUFT site. RPs are encouraged to work with reputable firms and to properly manage consultants to keep costs under control, ensure that established regulatory agency deadlines are responded to on time, and have a clear understanding of the project

objectives. Federal and state laws require every owner or operator of a petroleum UST to maintain financial responsibility to pay for any damages arising from operation of that UST. The roles and responsibilities of the consultant are discussed below.

## Consultant

The consultant is defined as a third party, generally a licensed and experienced professional geologist or civil engineer, hired by an RP to perform tasks associated with the investigation and remediation of a LUFT site. The intent of hiring a licensed professional is to ensure that the work required at a LUFT site is performed in accordance with the California Business and Professions Code (BPC) and other applicable laws and regulations. The consultant can also act as a neutral third party and address the contamination from a scientific perspective. It is important to note that, even though the regulatory agency may largely interact with the consultant, any directives issued by the regulatory agency are officially addressed to the RP. Non-compliance enforcement is also ultimately directed to the RP; however, RPs rely on consultants to meet their legal responsibilities, which are discussed in the RP section above.

Often, consultants are responsible for ensuring that field work is conducted in accordance with federal and state law. For further information, see the [Health and Safety](#) chapter of this Manual.

It is recommended that RPs sign contracts with reputable firms or individuals who have experience in LUFT investigation, risk evaluation, remediation, and site closure to protect an RP from paying too much for unnecessary work or from having to request addenda to work plans which were deemed “incomplete” or “not acceptable” by the regulatory agency.

## Regulatory Agency

A regulatory agency is any agency authorized to implement, administer, and enforce regulations. The regulatory agencies are responsible for representing the people of California. The agencies with a role in this program include the State Water Resources Control Board (SWRCB), the nine Regional Water Quality Control Boards (RWQCBs, Regional Boards), county-level Local Oversight Programs (LOPs), and county or city Local Implementing Agencies (LIAs).

### Agency Jurisdiction

Based on the nature of the LUFT release and its impact on human health, safety, and the environment, different agencies have jurisdiction over regulation of the site and, in some cases, jurisdiction is shared between agencies.

As stated in the 1989 *LUFT Field Manual*, the SWRCB and Regional Boards are responsible for protecting beneficial uses of water. Beneficial uses, which can be actual or potential, include municipal water supply, recreation, industrial water supply, and agricultural water supply. Therefore, the SWRCB and Regional Boards have jurisdiction over cases where there is a potential to impact groundwater quality or where groundwater quality has already been affected.

LOPs are contracted with the SWRCB to provide oversight of LUFT cases and are responsible for “soils only” and groundwater cases. When an LOP exists within the geographic boundaries of a Regional Board, the LOP is the lead agency and the Regional Board provides technical support when needed.

LIAs are sometimes health departments and often include divisions such as environmental health, occupational health, and hazardous materials management. Some health departments regulate USTs and may supervise soil and groundwater remediation. City and county fire departments and hazardous materials management offices also regulate USTs, supervise remediation, and have responsibility for fire and explosion prevention/ control at LUFT sites. Thus, local agencies usually have primary responsibility for inspection, leak detection, closure, and fire/public safety. In many instances, these agencies also supervise “soils-only” LUFT cases.

At times, agreements between local agencies and RWQCBs are established to allow local agencies regulatory authority over limited-extent, groundwater remediation LUFT cases. Regional Boards have the authority to supervise remediation at sites referred by local agencies and to provide approval for closure on cleanup cases where water quality is affected or threatened.

## Regulatory Agency Responsibilities

The role of these agencies is to verify that RPs follow applicable laws and regulations throughout the investigation and selected remediation processes.

Regulatory agencies’ primary legal responsibilities are to comply with the California H&SC and CCR, Articles 5 and 11:



- Send written Notices to Comply to RPs regarding violations.
- Concur the location, number, and depth of wells/borings/sample locations/etc. and the sampling frequency proposed by RPs and consultants.
- Receive and review electronic data submitted by RPs into GeoTracker.
- Ensure that cases are moving through the LUFT cleanup closure process in an effective manner.

Regulatory agencies are responsible for reviewing and approving all phases of work proposed in work plans submitted by RPs or consultants. Agencies are also responsible for reviewing all reports on LUFT cases to which they have been assigned.

Additionally, regulatory agencies have the authority to be present during site work, unless prior approval to proceed without an inspector onsite has been obtained. Regulatory agencies can reject analytical or field results obtained during field work if the proper inspection arrangements have not been made and there is a reasonable suspicion that the data are not valid. At times, regulatory agencies may require notice of UST inspection and remediation inspection, a minimum of three business days (or other agreed-upon interval among RP, consultant, and regulatory agency).

### Public Participation

The regulatory agency must inform the public about each confirmed unauthorized release that requires corrective action. This is typically satisfied once the site has been created in Geotracker (see [GeoTracker](#) chapter). Upon the completion of the corrective action, the regulatory agency shall give public notice if both of the following situations exists:

- 1) Implementation of the Corrective Action Plan (CAP) does not achieve the cleanup levels established in the Corrective Action Plan.
- 2) The regulatory agency does not intend to require additional corrective action, except for monitoring.

According to CCR Article 11, Section 2728, the public may be made aware of a confirmed unauthorized release in at least one of the following ways:

- 1) Publication in a regulatory agency meeting agenda.
- 2) Public notice posted in a regulatory agency office.
- 3) Public notice in a local newspaper.
- 4) Block advertisements.
- 5) Public service announcement.
- 6) Letters to individual households.
- 7) Personal contact with the affected parties by regulatory agency staff.

The regulatory agency shall comply with all applicable provisions of the California Environmental Quality Act (CEQA), Public Resources Code, commencing with Section 21000. LUFT sites are generally exempt from other CEQA requirements.

### Other Stakeholders

Other stakeholders have a role in LUFT cases. The adjacent property owners may have an interest because their property may potentially be contaminated. Community members may be interested because they want to know whether there are health and/or environmental risks to their community. Real-estate developers may have an interest when they have prospective projects planned for the site. Public meetings can be held with these stakeholders before a CAP is agreed on.

# UST Cleanup Fund

Version 1.0 - Draft August 2010



## Scope of This Chapter

This chapter describes the UST Cleanup Fund and explains its purpose, history, and application to UST sites in the State of California. This chapter is written for an audience with no prior knowledge of the Fund and is meant to aid responsible parties (RPs), consultants, and state and local regulators in their work on LUFT sites throughout the State of California.

The Barry Keene Underground Storage Tank Cleanup Fund Act of 1989 created the UST Cleanup Fund (USTCF, also known as "the Fund" – these terms will be used interchangeably in this document) to help owners and operators of USTs satisfy federal and state financial responsibility requirements. The Fund is administered by the Division of Financial Assistance (DFA) of the California State Water Resources Control Board (SWRCB) as a means of assisting UST owners and operators in meeting federal and state corrective action requirements.

The USTCF's mission is to contribute to the protection of California's public health and water quality through (1) establishing an alternative mechanism to meet financial responsibility requirements for owners and operators of petroleum USTs, and (2) reimbursing eligible corrective action costs incurred for cleanup of contamination resulting from the unauthorized release of petroleum from USTs. The Fund Regulations have been revised periodically in response to new legislation and to address issues not anticipated when the initial regulations were written.

## Statutes and Regulations

To fulfill the federal financial responsibility requirements specified in 40 *Code of Federal Regulations* (CFR), Part 280(H), the Fund is available to assist many thousands of individuals, small businesses, and corporations in meeting costs for the cleanup of contaminated soil and groundwater caused by leaking petroleum USTs. The federal financial responsibility requirements also require the Fund to provide coverage for third-party liability due to unauthorized releases of petroleum from USTs.

In addition to tank operators and owners, the Fund provides money to the Regional Water Quality Control Boards (RWQCBs) and Local Oversight Programs (LOPs) to abate emergency situations or to clean up abandoned sites that pose a threat to human health, safety, or the environment as a result of unauthorized petroleum releases from USTs.

**Legal.** The statutory authority for operation of the Fund and affiliated programs is contained in the California Health & Safety Code (H&SC), Chapters 6.75, 6.76, and 6.77. The most recent version of these code sections is dated January 2010.

The Fund regulations are contained in the California Code of Regulations (CCR), Title 23, Division 3, Chapter 18 (commencing with Section 2803). The current version of the Fund regulations is dated August 5, 2004.

UST Cleanup Fund staff members review reimbursement, budget, and pre-approval requests in accordance with the requirements of Section 2808.2(b) of the UST Cleanup Fund Regulations, CCR Title 23, Division 3, Chapter 18.

Established by Senate Bill (SB) 299 in 1989, USTCF statutes require every owner of a petroleum UST that is subject to regulation under H&SC Chapter 6.7 to pay a per-gallon storage fee. This fee, which began to accrue on January 1, 1991, began at \$0.006 and has risen to \$0.014 (as of late 2009) per gallon. In January 2010, the fee was increased to \$0.02 for a two-year cycle with the passage of Assembly Bill (AB) 1188 (Ruskin). The fee is collected by the State Board of Equalization (BOE) and normally generates about \$220 million per year for the Fund, with about \$150 million per year available for claim reimbursements. However, with the two-year increase in fees, it is projected that revenue will be increased by approximately \$50 million during fiscal year (FY) 2009-2010 and by \$100 million during FY 2010-2011.

The maximum amount of reimbursement per occurrence is \$1.5 million, minus any deductibles or settlement adjustments. The deductible amounts are set by statute and range from \$0 to \$40,000, based on the priority class of the claimant and any UST permit waivers. Since the USTCF's inception in the early 1990s, over \$2.5 billion have been reimbursed to eligible UST owners and operators to clean up soil and groundwater contamination in the State of California.

In the fall of 2007, an external Fund Stakeholder Review group was convened to discuss whether the Fund should be extended and, if so, whether any potential Fund improvements recommended by legislation, regulation, or internal

procedure would be adopted. After several meetings, the participants agreed that the Fund should be extended for 10 years and that the current fee (\$0.014 per gallon) should not be changed. Following the 2007 review, a Consensus Report was prepared and distributed. In February 2008, legislation was introduced proposing the extension of the Fund. On September 30, 2008, the bill (SB 1161, Lowenthal) was signed by the Governor, extending the Fund until January 1, 2016.

**Legal.** On May 19, 2009, the SWRCB passed Resolution No. 2009-0042. This resolution initiated a series of reviews of the UST program, including the Fund. One of the requirements of this resolution was that a Task Force be created to make recommendations for improvements to the USTCF administrative procedures and to improve the UST Cleanup regulatory program. As a result, an audit was conducted at the Fund.

More information on the Task Force created to make recommendations for improvements to the Fund and results of the audit can be found on the Fund's web site:

[http://www.waterboards.ca.gov/water\\_issues/programs/ustcf/taskforce.shtml](http://www.waterboards.ca.gov/water_issues/programs/ustcf/taskforce.shtml)

## Fund Cost Guidelines

The Fund Cost Guidelines have been developed pursuant to H&SC Section 25299.57(h). This summary of expected costs may be used by claimants as a guide in selecting and supervising consultants and contractors.

[http://www.waterboards.ca.gov/water\\_issues/programs/ustcf/technicalformsinfo.shtml](http://www.waterboards.ca.gov/water_issues/programs/ustcf/technicalformsinfo.shtml)

The primary purpose of the Fund Cost Guidelines is to provide direction to claimants for evaluating proposed and incurred corrective action costs at sites eligible for participation in the Fund. Specifically, these guidelines are intended to help claimants identify reimbursable goods and services and understand how the Fund evaluates activities and costs. Claimants will also be able to judge whether additional justification will likely be required to support given costs, or whether a call for assistance from the Fund is in order.

The guidelines do not establish reimbursement limits for the listed items and activities. They are not intended to remove the element of competition or freedom of choice from the industry, meaning that competitive bidding for work performed at a LUFT site is encouraged.

## 5-Year Review

H&SC Section 25299.39.2(a) requires the Fund to review the case history of each claim having a Letter of Commitment (LOC) active for more than 5 years annually, unless the owner or operator objects to the review. This is known as the 5-Year Review.

The purpose of the 5-Year Review is to determine whether a recommendation for case closure is in order, or if alternative actions are appropriate. Aside from being required by law, this review is beneficial to small businesses and individuals because it provides for an additional party to check on the progress of the case relative to the expenditure of funds and reduces the chance that the RP will run out of funds before the case is cleaned up. It also provides an opportunity for the Fund to track cases and better facilitate work to achieve site closure.

The Fund's 5-Year Review Unit reviews site case history and directives to make one of the following recommendations:

- 1) Recommend the site for closure.
- 2) Concur with the current corrective action activities.
- 3) Recommend modification to the current corrective action(s).

It is the responsibility of the lead regulatory agency to respond to the recommendation made by the 5-Year Review Unit as to the path forward based on the recommendation.

If the RP believes that closure is warranted, it is recommended that the consultant assemble a comprehensive closure request package for submittal to the lead regulatory agency. If the closure request is denied by the lead regulatory agency, the RP may petition the SWRCB for case closure.

## Cost Pre-Approval

In order to expedite payment processing time, the Fund has historically pre-approved estimated corrective action costs to ensure that costs are eligible, reasonable, and necessary. Cost pre-approval was suspended in 2003 due to Fund staffing reductions, and was resumed in FY 2006-07.

During 2010, cost pre-approval will be converted to a budget approval process. Budgets will be established for all planned activities for a case covering a 12- to 18-month period. The budget format will be structured around eight work phases, applicable sub-tasks for each phase, and projections for all activities to be conducted during each quarter. For efficiency in processing, reimbursements will be structured to correlate with the budget format. Finally, it will be required—through a consultation process involving the claimant, consultant, regulator, and Fund staff—that all activities proposed in the budget fit into the overall road map to closure, based on the most current conceptual site model.

**Help!** For more information about how to file a closure petition or other UST-related petition, go to:

[http://www.waterboards.ca.gov/water\\_issues/programs/ust/cleanup/petitions.shtml](http://www.waterboards.ca.gov/water_issues/programs/ust/cleanup/petitions.shtml)

For the most recent update on the availability of funding, refer to:

[http://www.waterboards.ca.gov/water\\_issues/programs/ustcf/paymentformsinfo.shtml](http://www.waterboards.ca.gov/water_issues/programs/ustcf/paymentformsinfo.shtml)

The Fund website also has materials for Pre-Approval requests, including the necessary forms and instructions. To submit a Pre-Approval request (for preparation of a closure request report) or for other related activities, see:

[http://www.waterboards.ca.gov/water\\_issues/programs/ustcf/docs/cost\\_preapproval/costpreapproval.pdf](http://www.waterboards.ca.gov/water_issues/programs/ustcf/docs/cost_preapproval/costpreapproval.pdf)

For technical information, please visit the Fund website and select Technical Information from the left-hand column under USTCF Resources:

([http://www.waterboards.ca.gov/water\\_issues/programs/ustcf/technicalformsinfo.shtml](http://www.waterboards.ca.gov/water_issues/programs/ustcf/technicalformsinfo.shtml))

### Further Reading.

Each fiscal year, the Fund prepares a “Legislative Annual Report,” which provides a performance summary of the Fund’s activities. This information comes from the previous fiscal year’s status on claims received and reimbursed, in addition to other historical data. This report also provides a useful summary of the major legislative changes to the Fund since its inception.

[http://www.waterboards.ca.gov/water\\_issues/programs/ustcf/legannualreports.shtml](http://www.waterboards.ca.gov/water_issues/programs/ustcf/legannualreports.shtml)

### References

USTCF (the Fund) website:

[http://www.waterboards.ca.gov/water\\_issues/programs/ustcf/](http://www.waterboards.ca.gov/water_issues/programs/ustcf/)



# GeoTracker

Version 1.0 - Draft August 2010



## Scope of This Chapter

This chapter presents GeoTracker, the State Water Resources Control Board (SWRCB) database and explains its required use in the cleanup process of Leaking Underground Fuel Tank (LUFT) sites. It describes the history behind the development of GeoTracker, and the goals associated with GeoTracker's use. The responsibilities of various relevant parties are defined in regards to GeoTracker.

## Background

GeoTracker is an on-line database and geographic information system (GIS) that (1) provides access to statewide environmental data and (2) tracks regulatory data for the following types of sites:

- 1) LUFT cleanup sites,
- 2) Cleanup Program Sites (CPS; also known as Site Cleanups [SC] and formerly known as Spills, Leaks, Investigations, and Cleanups [SLIC] sites),
- 3) Military sites (consisting of: Military UST sites; Military Privatized sites; and Military Cleanup sites [formerly known as DoD non-UST]),
- 4) Land Disposal sites (Landfills), and
- 5) Permitted UST facilities.

**Legal.** AB 2886, enacted in September 2000, authorized the SWRCB to establish electronic formats for reporting compliance data and mandated the adoption of a single standard for electronic reporting of analytical data from certified analytical laboratories. On April 26, 2001, the SWRCB adopted regulations to implement AB 2886, which required electronic submittal of soil and/or water analytical data and survey data to GeoTracker. On September 30, 2004, the SWRCB adopted regulations (Chapter 30, Division 3 of Title 23, CCR, and Division 3 of Title 27, CCR) which required electronic submittal of information (ESI) for LUFT, SLIC, DOD, and Landfill groundwater cleanup programs. These regulations also added new Data Dictionaries (the format for electronic data submittals) to CCR Title 27, in coordination with existing California Environmental Protection Agency (Cal/EPA) Unified Program Data Dictionaries.

## Purpose of GeoTracker

The purpose of GeoTracker is to allow interested parties to obtain graphical and textual information about any LUFT, UST, Aboveground Storage Tank (AST), CPS, military site, landfill, or permitted UST facility by entering a site address, partial site address, or site name into the database. Additionally, GeoTracker provides on-line tools to analyze potential threats to drinking-water sources. GeoTracker uses customized screens and data-management tools to provide users access to site information and data over the Internet and to view site locations on a map display.

GeoTracker has both public and secure pages/screens:

- <http://geotracker.waterboards.ca.gov> (public)
- <https://geotracker.waterboards.ca.gov/regulators> (regulators)
- <https://geotracker.waterboards.ca.gov/esi> (responsible parties [RPs] and/or their agents)

## Benefits of Electronic Reporting

The implementation of electronic reporting has provided benefits for both the SWRCB and the public. Electronic reporting:

- Provides decision-makers with accurate, up-to-date, accessible, and *complete* statewide information concerning cleanup sites where there has been a chemical release.
- Enhances the capabilities of the SWRCB, Regional Water Quality Control Boards (RWQCB), and local regulatory agencies in monitoring and assessing the contaminant threat to drinking-water wells.
- Facilitates public access to information: instead of having to physically travel to a government building to review a paper copy of the case file, concerned individuals can review and analyze information over the Internet.



### Laboratory Data

Analytical data (including geochemical data) for all soil, vapor, and water samples collected for the purpose of subsurface investigation or remediation are required to be uploaded into GeoTracker in the specified Electronic Deliverable Format™ (EDF) described at:

[http://www.waterboards.ca.gov/ust/electronic\\_submittal/docs/edf\\_gr\\_v1\\_2i.pdf](http://www.waterboards.ca.gov/ust/electronic_submittal/docs/edf_gr_v1_2i.pdf)

The EDF is a comprehensive data standard designed to facilitate the transfer of electronic data files between data producers and data users. Laboratories can produce the Laboratory Electronic Deliverable Format™ (LAB EDF) electronic data deliverable (EDD) (hereafter referred to as EDF) using the U.S. Army Corps of Engineers Loading Tool (COELT) software or software programs other than COELT (e.g., Laboratory Information Management System [LIMS] software).

The EDF components for laboratory data include:

- Chain-of-Custody Information
  - Sample collection information
  - Administrative information
  - Preservatives added to the samples
  - Conditions of transport
- Laboratory Results Information
  - Tests performed
  - Parameters tested
  - Analytical results
- Quality Assurance (QA) Information (key to data verification)
  - Detection limits
  - Control limits for precision and accuracy
  - Narrative report explaining non-conformances
- Built-in Guidelines and Restrictions
- Valid Value Lists (VVLs)

### Technical (Compliance) Reports

Remediation and Monitoring Reports for contaminated soil, soil-gas, or groundwater sites are required to be uploaded to GeoTracker in PDF format. These reports should include the signed transmittal letter, professional certification, and all collected data.

### Boring Logs and Well-Screen Intervals

Boring logs prepared by an appropriately registered professional must be uploaded into GeoTracker in PDF format. If a monitoring well is installed, the screen depth (measured in feet from the top of casing to the beginning of the screened interval) and the length of the screened interval (also in feet) must be entered into GeoTracker when the well is added as a new Field Point Name to the site's online list of Field Point Names.

### Depth-to-Water Data

Depth-to-water information for monitoring wells (the measured depth from the top-of-well-casing to the groundwater surface, reported to the nearest hundredth [0.01] of a foot) must be uploaded to GeoTracker whenever the data are collected, even if the well is not actually sampled during a given sampling event. Drinking-water wells generally do not need

to have their depths to water reported unless they are surveyed as permanent sampling points (a “permanent sampling point” is defined as a well location that is sampled for more than a 30-day period).

## Locational Data

If samples from permanent sampling points are included in a report to a regulatory agency as part of a cleanup program, these sampling point locations must be surveyed to 0.01 foot accuracy. These typically include any groundwater or similar monitoring points at the site or any drinking-water wells that are included in the regulatory report. The surveyed location coordinates for these permanent sampling points must be uploaded to GeoTracker in geographic format (longitude / latitude). Transient or one-time sampling points (e.g., direct-push technologies, piezometers, grab samples, soil borings, stockpile samples, etc.) do not need to be surveyed.

## Elevation Data

The elevation at the top of casing for all permanent groundwater monitoring wells must be uploaded to GeoTracker. Drinking-water wells included in the report do not need to have top-of-casing elevation reported unless they are identified as permanent sampling points (i.e., are sampled for more than a 30-day period).

## Site Map

An electronic, generalized site plan map must be uploaded to GeoTracker. The site map should display buildings, tank locations (including former tank locations), dispenser islands, streets bordering the facility, monitoring well locations, boreholes, and all other sampling locations where soil, water, and vapor samples have been collected. The site map is uploaded as a stand-alone document and may be submitted in GIF, TIFF, JPEG, or PDF format. Additional updated site maps may be submitted at any time.

### Help!

The process of how to claim a site, how to format and upload data, and other technical information can be found under the “Electronic Submittal of Information” links at [http://www.waterboards.ca.gov/ust/electronic\\_submittal/index.shtml](http://www.waterboards.ca.gov/ust/electronic_submittal/index.shtml).



### Non-Regulatory Stakeholders

#### Responsible Party (RP)

The RP has two primary electronic reporting responsibilities: (1) “claiming” their site(s) in GeoTracker, meaning the RP takes responsibility for the uploading of required documentation and (2) uploading ESI compliance data and reports. If the RP chooses not to upload ESI compliance submittals personally (typically the RP does not do the uploading), they may delegate all or a portion of the upload duties to an “Authorized RP Agent” and/or may grant secondary upload access to Contractors and/or Laboratories. Only RPs and authorized RP agents can grant secondary access to Contractors and Laboratories.

In order to claim a site, the RP (or an Authorized RP Agent acting on the RP’s behalf) must create a GeoTracker account, if the RP doesn’t already have one. The RP then logs onto their GeoTracker account and searches for the site using the “Request Additional Facilities” option. Once the site is found, the RP places a checkmark in the “Add” box and clicks on “Request Checked Facilities” to request the site (**note:** after requesting the site, Authorized RP Agents must also fax the Authorization Form signed by the RP to the SWRCB). If assistance is needed, the GeoTracker Help Desk can be contacted via email at: [geotracker@waterboards.ca.gov](mailto:geotracker@waterboards.ca.gov) or via telephone at (866) 480-1028.

Once the request for the site has been approved by the SWRCB, the RP will have successfully met the prerequisite regulatory compliance requirement to “claim” the site.

#### Authorized RP Agent

An Authorized RP Agent is typically an environmental consulting firm whom the RP has designated to act on their behalf in fulfilling the RP’s GeoTracker electronic reporting responsibilities. The RP can still create a personal GeoTracker RP account, even if they choose to designate an Authorized RP Agent to act on their behalf.

If they so choose, Authorized RP Agents can do all of the required ESI compliance uploading on behalf of an RP without any contractors or laboratories having to perform uploads. Instructions for claiming a site on behalf of the RP are under the “Responsible Party” section.

**Important!** For all open cases, timely upload of all responses to corrective action requests and of all other required electronic submittals **is required by law**. Corrective action responses are not considered complete until all other required electronic submittals have been uploaded. The RP is out of compliance if the open case is not claimed in GeoTracker and the required information is not uploaded into GeoTracker; this can make a UST Cleanup Fund (USTCF) site ineligible for reimbursements until that site is brought into compliance with GeoTracker data requirements. The RP is ultimately responsible for making sure that an open case is in regulatory compliance.

#### Contractor

An RP (or an Authorized RP Agent) may employ a number of Contractors to collect samples, perform groundwater measurements, survey locations and elevation, upload data and reports, and manage data for facilities or cleanup sites. To gain access to an RP’s GeoTracker site, a contractor logs onto their GeoTracker “Contractor” account, and request access to the site (the RP or Authorized RP Agent must already have successfully “claimed” the site for this process to function). After the Contractor requests access to the site, the RP or Authorized RP Agent must then log onto his/her own account and approve the Contractor’s request for access.

#### Laboratory

The Laboratory is responsible for sample analysis and for providing the RP, Authorized RP Agent, or Contractor with data in EDF format, ready for GeoTracker upload and, in some cases, in hard-copy report format also.



In the vast majority of cases, RPs (and Authorized RP Agents) do not ask the laboratory to be responsible for uploading the EDF directly into the GeoTracker system. Typically, after performing an online error check, the Laboratory forwards the EDF files to the RP/Authorized RP Agent/Contractor, who reviews them to ensure the validity of the EDF data and then uploads the files to the SWRCB GeoTracker database.

In some cases, the RP (or Authorized RP Agent) may wish to have the laboratory submit the EDF data directly to GeoTracker. In these instances, the laboratory must first gain upload access to the site, in the same way that Contractors gain access: by logging onto their own GeoTracker “Laboratory” account and requesting access to the site. The RP or Authorized RP Agent then logs onto their own account and approve the Laboratory’s request for access.

Please note that GeoTracker Contractors *cannot* grant a Laboratory access to a site; only RPs and Authorized RP Agents can do so.

## Regulatory Agencies

### State Water Resources Control Board

The SWRCB is responsible for the overall operation and maintenance of the GeoTracker system and its successful use by all entities involved with soil and groundwater contamination issues. The SWRCB is also responsible for approving RP and Authorized RP Agent requests for upload access to facilities. Further responsibilities of the SWRCB include providing guidance and tools to standardize the review and quality of electronic compliance data submitted and maintaining user accounts for RPs, consultants, and regulatory agencies.

### Lead Agency Caseworker

The lead agency caseworker (whether from the RWQCB, Local Oversight Program [LOP], or Local Implementing Agency [LIA]) receives electronic data submitted by the RP or his/her consultant(s). This “receipt of data” includes reviewing the Field Point Names in the EDF (to verify whether names in the hard copy report match those in the electronic data) and noting whether the PDF of the hard-copy report has been uploaded to the GeoTracker regulator pages. Once the data have been “received,” they are moved into the GeoTracker archive database and made available to the public.

The lead regulatory agency oversees the RP to ensure current and accurate data is uploaded to GeoTracker. The accuracy, completeness, and timeliness of the data are critical because:

- 1) The data are used by the public to understand the conditions of sites,
- 2) The data are used by the real-estate industry to assess the value of sites and surrounding property,
- 3) The data are used by the state and federal government to make decisions related to priorities and funding, and
- 4) The data are used by the Office of Management and Budget, Congress, U.S. Environmental Protection Agency (USEPA) headquarters, and USEPA Region 9 to evaluate the effectiveness of the program.

Efficient use of GeoTracker by lead regulatory agencies can increase overall effectiveness in managing their caseloads. All incoming and outgoing documents related to a LUFT site are included in GeoTracker, which makes them available to the public, other agencies, RP(s), and consultants and/or contractors who may work on the case. The regulator can effectively track incoming documents by their due dates and receive reminders when a document is past due. Used in this manner, GeoTracker assists in moving toward paperless case management.

Lead regulatory agencies are requested to ensure that all their open LUFT cases are properly claimed by RPs (or, alternatively, by their authorized RP agents) and that data for open cases are being submitted regularly. Additionally, lead agencies ensure that the proper case status for each site is correctly entered into GeoTracker and updated as the case status changes (e.g., assessment, remediation, closure).

## Assistance with Use of GeoTracker

**Help!** Considerable documentation and guidance regarding GeoTracker are available at the State Water Board GeoTracker ESI web page:  
[http://www.waterboards.ca.gov/ust/electronic\\_submittal/index.shtml](http://www.waterboards.ca.gov/ust/electronic_submittal/index.shtml)

# Health and Safety

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## Scope of This Chapter

This chapter presents health and safety considerations for leaking underground fuel tank (LUFT) sites. It describes the need to incorporate worker and community health and safety into the LUFT cleanup process. This chapter is intended to provide a number of items to consider when preparing for and conducting field work at a LUFT site; however, the information in this chapter is not intended to be all-inclusive, as it is recognized that each organization has its own health and safety program and takes responsibility for the health and safety of the activities conducted by its employees.

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## Overview

Health and safety must be considered a priority in planning and implementing site activities. Recommended safety precautions, per Occupational Safety and Health Administration (OSHA) guidelines, can be used to protect associated parties and the environment and avoid both present and potential hazards. Actions should be documented as required by federal, state, and local regulations.

## Safety Considerations

There are many worker and public health and safety issues to be considered during any activities conducted at a LUFT site. These issues include:

**Transportation to and from the LUFT Site.** It should be realized that there is the potential for a vehicular accident while driving to and from the site.

**Mobilization and Demobilization.** Traffic hazards should be considered when setting up the field support zone. It is recommended that workers wear high-visibility safety vests.

**Personal Protective Equipment.** It is important that workers at LUFT sites have the correct personal protective equipment (PPE).

**Training.** It is important that workers at LUFT sites have the proper training, including OSHA Hazardous Waste Operations and Emergency Response (HAZWOPER) training. More information regarding OSHA requirements is provided in the Worker Health and Safety Plan section below.

**Dust.** It is important to minimize potential exposure to dust generated as a result of the proposed activities. Control methods include covering sources, misting sources with water using stationary sprayers or water trucks, and halting activities altogether.

**Noise.** It is important to minimize the impact of noise to the workers onsite and occupants of neighboring properties. Make sure that occupational noise exposure standards and specifics regarding noise in 29 CFR 1910 are being met in the relevant Health and Safety Program. Note that noise ordinances are generally enforced from 7:00 p.m. to 7:00 a.m. on weekdays, depending on the jurisdiction and zoning. Weekend work is discouraged, and noise standards may be more stringent during the weekend. Nearby residents will appreciate any efforts to minimize noise generated by site activities.

**Open Excavations.** These are a risk to both workers and the public; secure fencing is recommended if excavations cannot be backfilled at the end of the work day. During excavation activities, the use of caution tape with delineators is recommended to avoid accidents near the excavated area. If workers need to enter the excavation area for any reason, shoring may be required; OSHA, state, and local regulations regarding shoring of excavations should be ascertained. Workers and onlookers who are not directly involved with the project must remain outside the enclosed area.

**Buried Utility Lines.** Underground utility lines present a significant risk when excavation activities are planned at a LUFT site. It is important to provide proper notification to the local utility company. Areas with buried utility lines can be located and marked by dialing 811 or 1-800-227-2600, *Call Before You Dig!*, a free, California utility-locating service. For confirmation, use of a private utility clearance company is also recommended.

**Overhead Electrical Lines.** Overhead electrical lines are a threat at a LUFT site when drill rigs, cranes, and excavators are used. If overhead lines are present, call the utility company and find out what voltage is on the lines. Ask whether the utility company can shut off the lines while work is taking place near them. If overhead lines cannot be shut down, ask the utility

company whether it can install insulation over the lines during the time work will be taking place near them. Inform workers of overhead utility hazards and the precautions to prevent contact. Ensure that workers are not placed in dangerous proximity to high voltage by using a spotter, placing warning decals on equipment and drill rigs regarding the 10-foot minimum clearance, and conspicuously marking and maintaining marks of the location of overhead utilities. Consider overhead lines energized (“hot,” “live”) until the local electric utility indicates otherwise.

**Important! LOOK UP! BEST SAFETY PRACTICE: NEVER GET CLOSER THAN 10 FEET FROM AN OVERHEAD POWER LINE!**

**Stockpiled Soil.** Stockpiled soil that has been staged for land farming or removal represents a potential hazard to the public and the environment if stockpiled soils are contaminated. This safety risk is best minimized by containing and covering stockpiles to prevent runoff and vapor or dust exposures, and by locating such stockpiles in a secured area of the site to prevent public exposure.

**Vapors.** Good site health and safety practices include minimizing public exposure to potential vapor emissions resulting from site activities and monitoring hazardous atmospheres for workers while they conduct activities at a LUFT site. Engineering and construction practices which typically reduce such emissions include the following: pumping out non-aqueous-phase liquids (NAPL); covering off-gassing excavations or stockpiles; backfilling off-gassing excavations with clean, non-impacted fill; using soils that have been stockpiled as backfill after receiving field confirmation (using field instrumentation) that the excavated soil is no longer off-gassing detectable vapors; misting excavations or stockpiles with water; covering excavations or stockpiles with foam or other vapor-suppressing agents; locating stockpiles away from and/or downwind of public receptors; and stopping work.

**Explosion and Fire Hazard.** The potential for explosion or fire hazards is of real concern at LUFT sites, due to the nature of working with petroleum products. It is important to properly monitor tanks, excavations, open areas, and enclosed spaces with a combustible gas indicator (CGI). An explosive environment is one containing 20% or greater of the Lower Explosive Limit (LEL). Spark and ignition sources should be avoided when an explosive environment is possible.

**Stormwater.** The consistent use of Best Management Practices (BMP) is intended to control surface runoff in order to prevent or minimize the transport of pollutants to receiving waters. Practices include, but are not limited to, the use of hay bales, hay socks, sand bags, and high-density polyethylene plastic to cover inlets. In some cases, a National Pollutant Discharge Elimination System (NPDES) permit may be required.

**Investigation-Derived Waste (IDW).** IDW is an additional hazard that may be present at LUFT sites. IDW can be different media, including (but not limited to) soil, water, and sludge. Refer to various guidance on management of IDW, such as the USEPA Guide to Management of Investigation-Derived Wastes (available online at <http://www.epa.gov/superfund/policy/remedy/pdfs/93-45303fs-s.pdf>).

## Worker Health and Safety Plans

**Legal.** Federal and State regulations require HASPs for field activities where hazardous substances may be encountered. Language found in 29 *Code of Federal Regulations* (CFR) §1910.120 establishes Federal requirements for HASPs and training.

29 CFR §1910.120 can be obtained from the U.S. Government Printing Office website:

[http://edocket.access.gpo.gov/cfr\\_2008/julqtr/pdf/29cfr1910.120.pdf](http://edocket.access.gpo.gov/cfr_2008/julqtr/pdf/29cfr1910.120.pdf)

OSHA requires a site-specific HASP for intrusive or other field-related work and requires that each HASP be appropriate for the proposed work. If the scope of work changes, a revised HASP may be required (to remain in compliance with OSHA regulations) before work is allowed to proceed.

Individuals working on or visiting a site in an official capacity must study the HASP before beginning any field activities. They must also familiarize themselves with the emergency telephone numbers within the HASP, any hazards which may be encountered, and the corresponding emergency response plan. A copy of the current version of the HASP must be available onsite during site activities. Each person involved in the work will attest, by signing the HASP, to the fact that he or she understands the hazards which may be involved, is familiar with the emergency procedures to be followed in case of an accident, and has the proper training for the tasks to be performed.

Site safety meetings to review the scope of the scheduled work, the pertinent safety concerns, and the relevant emergency procedures are held each day before work begins. Everyone who will participate in field activities that day attends this “tailgate meeting.”

The following are the minimum OSHA requirements for inclusion in an acceptable HASP:

- A list of the hazardous materials that may be encountered, and decontamination procedures and/or required emergency treatment for each material listed.
- A Material Safety Data Sheet (MSDS) should be available for hazardous materials used or stored onsite.
- An Activity Hazard Analysis (AHA), also known as a Job Safety Analysis (JSA), needs to be included for each activity that will be conducted at the site. This will include the potential hazards associated with each of the work activities.
- Name and job function (e.g., site geologist, driller, etc.) of the Site Safety Officer.
- Name and job function of the alternate Site Safety Officer.
- Name and job function of other responsible site personnel and their alternates.
- Addresses and phone numbers for the nearest emergency response facilities:
  - Fire Station
  - Ambulance Service
  - Police
  - Emergency Health Facility
  - Poison Control: 1-800-222-1222
- A map showing the most direct route to the nearest emergency health facility. This map must be at a scale that is easily read, and the route clearly identified, so that a person not familiar with the area can locate the facility with minimum delay. The map should be placed in a location that can be easily seen by workers, should an emergency be encountered.
- A narrative paragraph describing how to drive to the nearest emergency health facility, i.e., which roads, turns, and directions (left or right, and the approximate distance) are to be taken.
- **Hazard Communication Plan:** This includes addresses and telephone numbers for the responsible parties (RPs) and regulatory agencies to which accident reports must be provided, and the lines of communication for reporting a hazardous incident. The parties may include, but are not limited to:
  - *Federal Government:* U.S. Environmental Protection Agency (USEPA), OSHA, Centers for Disease Control (CDC), U.S. Coast Guard (USCG), etc.
  - *State Government:* California Environmental Protection Agency (Cal/EPA), California Department of Toxic Substances Control (DTSC), Regional Water Quality Control Board (RWQCB), etc.
  - *County/City Government:* Department of Environmental Health (or relevant county/city office), air pollution control district (APCD), etc.
  - *RP and RP consultant(s).*
- Work-zone delineation, e.g., work zone, support zone, decontamination zone, restricted access zone, etc.
- Level of PPE required. If different work activities require different levels of protection, the requirements for each must be specified. For cases where Level A, B, or C is appropriate, workers must be trained in the use of the PPE required. No worker with facial hair which might prevent the tight fit of a respirator mask is to be assigned to tasks requiring Level A, B, or C PPE.
- Traffic control and site-access control procedures.
- Air monitoring procedures and safety limits.
- Procedures for managing weather-related problems, e.g., lightning, heavy rain, excessive heat, cold, wind, etc.
- Location of emergency equipment, such as fire extinguishers, vapor-suppressant applicators, etc. The individuals trained in and assigned to their use must be named and must be aware of their responsibilities.

## Community Health and Safety Plans

Some regulatory agencies require that a Community HASP be included in the work plan in situations where public health and safety may be at risk. It is the responsibility of property owners, RPs, consultants, and subcontractors to conduct on-site activities in such a manner as to avoid the creation of any public health and safety hazards or nuisances. Precautions

and continuing care to prevent impacts to the surrounding community are an ever-present concern, even in the absence of a Community HASP. If there will be significant noise or any risk to the community, at a minimum, a notice should be sent to community members who will be directly impacted.

## References

29 *Code of Federal Regulations* (CFR) §1910.120, re. Federal requirements for HASPs and for hazardous-materials training. USEPA 1992. Guide to Management of Investigation-Derived Wastes. January 15, 1992.

USEPA. 1992. Guide to Management of Investigation-Derived Wastes. April 1992. Available at <http://www.epa.gov/superfund/policy/remedy/pdfs/93-45303fs-s.pdf>

# Work Plans

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## Scope of This Chapter

This chapter presents good practices for creating work plans used during the various phases of work at LUFT sites. Elements of various work plans and the work plan approval process are discussed.

### Introduction

A work plan is a technical document that outlines both the scope of work (SOW) to be completed at a LUFT site and how the SOW is expected to be completed. The work plan is also used to ensure that all parties clearly understand and agree on the SOW to be completed. A work plan provides sufficient information to allow the lead regulatory agency to evaluate the reasonableness of the proposed work.

Work plans are written for a variety of activities (e.g., over-excavation, well installation, well destruction, receptor surveys, etc.), and specific work plans are required for each type of event, depending on direction received from the lead regulatory agency.

#### Legal.

California Code of Regulations (CCR) Title 23, Division 3, Chapter 16, §2722, "Scope of Corrective Action," requires that a work plan be submitted to the regulatory agency for review and comment prior to implementing any phase of investigation or corrective action associated with regulated UST systems. These laws require work plans for the following activities:

- Post-tank-removal corrective actions
- Interim remedial actions
- Preliminary site assessments
- Soil and groundwater investigations
- Corrective action plans
- Verification monitoring programs

### Work Plan Approval Process

When a lead regulatory agency requests that an RP undertake an action at a LUFT site, it is the responsibility of the RP to prepare a work plan that provides the details of the activities to be implemented. The work plan should include a schedule and timeline, and should be completed in the time allotted for its completion. In most cases, the RP's authorized agent/consultant will prepare the work plan on behalf of the RP. The work plan is to be submitted to the lead regulatory agency for review.

- **Upon approval of the work plan**, work can begin and progress as scheduled unless the deadline will not be met, in which case the RP needs to request written permission for an extension and justification for the extension as soon as it becomes apparent the deadline will not be met. After work is complete, the RP submits a report stating that the work is complete.
- **If the original work plan is not approved**, the regulatory agency identifies the specific elements of the work plan that are not approved and explains why they are not approved. The RP modifies the work plan as necessary and resubmits it to the regulatory agency.

The RP may begin implementation of the work plan 60 calendar days after submittal, unless the RP is otherwise directed in writing by the regulatory agency. Before beginning these activities, the RP must:

- **Notifies the regulatory agency** of the intent to initiate the actions proposed in the submitted work plan.
- **Complies** with any reasonable, appropriate, and technically justified conditions set by the regulatory agency, including mitigation of adverse consequences from the cleanup activities.



### **Important!**

Even though an RP may begin work 60 days after a work plan has been submitted regardless of whether the agency has issued approval, site work conducted without appropriate authorization may not be accepted by either the regulatory agency (e.g., the work is not technically defensible) or the UST Cleanup Fund (e.g., the work was not justified, or was not conducted in the most cost-efficient manner).

# Work Plans for Site Assessment

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## Site Assessment Work Plans

There are two types of work plans used during site assessment: **fixed** and **dynamic**.

When a **fixed work plan** is utilized, the consultant/ responsible party (RP) determines exactly where sampling will occur, how many samples will be collected, and the duration of the investigation. This is referred to as a “multiple-phase approach” to site assessment. The benefit of this type of work plan is that the stakeholders know the cost of the project and exactly which tasks will be conducted (with the exception of slight field variances). The drawback to this type of work plan is that, as the field sampling occurs, new issues may arise, but the consultant/RP cannot collect further samples because they have not been approved by the regulator in the work plan.

When a **dynamic work plan** (referred to as the “the Triad Approach” by the USEPA) is utilized, all stakeholders agree to certain field sampling procedures and general sampling locations, but modify the sampling based on field conditions. This is referred to as a “single-phase approach” to site assessment. Because of the dynamic nature of this type of work plan, the overall process can be expedited, but the exact cost of the investigation is unknown prior to heading into the field.

## Elements of a Fixed Work Plan

The following elements should be considered when developing a fixed work plan. Each work plan will vary based on the necessary activities and should be specific to site conditions. The level of effort and details in a particular work plan are determined by the responsible professional in charge of the investigation, with input from regulatory agencies as appropriate.

### Proposed Work and Technical Approach

The proposed work needs to include details such as proposed sample locations, number of samples, analyte list for samples, field quality control (QC) samples, laboratory QC samples, and justification for the proposed work in sufficient detail to allow the regulatory agency to evaluate the reasonableness of the proposed work and whether it will be performed in accordance with accepted practices.

The work plan describes anticipated methodologies and procedures. It is recommended that Standard Operating Procedures (SOPs) be included as an appendix to the work plan. If there are any planned deviations from accepted practices, it is recommended that reasons for their selection be provided. Methodologies and procedures for work plans include, but are not limited to:

- Underground utility locating,
- Drilling,
- Well construction and development (if monitoring wells are, will be, or are expected to be installed),
- Sampling, and
- Decontamination of sampling tools.

The work plan indicates how the analytical results will be evaluated and provides an estimated timeline for completion of the work.

### Assumptions

This discussion in the work plan includes identifying and justifying any and all assumptions made in the work plan.

### Analytes and Methods

The target analytes and analytical methods to be used at a LUFT site are described in the [Laboratory Analysis and Methods](#) chapter of this Manual.

### Reporting Requirements

This section describes the anticipated reporting procedures for the findings from the work to be conducted. Reports are discussed in more detail in the [Reports](#) chapter of this Manual.



## Performance Measures

It is important for the consultant performing the work at the site to document site activities. This discussion in the work plan should clarify how the proposed work will move the site toward closure and how performance will be monitored and documented.

## Elements of a Dynamic Work Plan

The majority of the information presented in this section was extracted from “USEPA Guidelines for Dynamic Work Plans” (USEPA 2001).

Elements to consider for incorporation into dynamic work plans include:

### Systematic Planning

Create clearly stated goals and objectives, and define scientifically and legally defensible site decisions using a well-rounded technical team and stakeholder input. Extensive planning is performed to help the field team prepare for the challenges that may arise during site assessment and to ensure that the team will not be thwarted by obstacles that arise during the site visit. It is important for all stakeholders to be in agreement on the approach prior to the commencement of site activities.

### Use of a Conceptual Site Model (CSM)

The CSM should be used to determine data gaps and to make decisions regarding sampling at the site; it should be updated as soon as new data are gathered.

### On-Site Generation of Data

Real-time analytical methodology is used to provide qualitative and semi-quantitative data. When data are generated immediately, site decisions can be made efficiently and the sampling strategy can be adjusted according to the new data.

High-quality quantitative data can be obtained from a wide variety of rugged field analytical equipment and from mobile laboratories. Any mobile laboratories used in California are required to be certified by the Environmental Laboratory Accreditation Program (ELAP).

### Immediate Decision-Making Capability

The on-site generation of data helps define hot spots and can assist in determining whether the removal or treatment of contaminated media is preferable, while minimizing the collection and analysis of uninformative samples as well as determining risk to human health and the environment.

### Adaptive Sampling and Analysis Strategy

As data results are either generated or received, a strategy for making decisions must already be in place. Also, as sampling data are obtained, the established CSM is evaluated for accuracy. It is extremely important that goals and objectives be clearly defined, because the constant flow of decisions that need to be made will be based on the goals and objectives of the work.

For additional information, see the USEPA guidelines at <http://www.epa.gov/tio/download/char/dynwkp1n.pdf>.

## Pros and Cons of Dynamic Work Plans

Advantages of dynamic work plans include:

- Site assessment can be accomplished more rapidly.
- The cost of field work is often reduced because the process is condensed.
- The number of borings may be reduced because real-time feedback of analytical results facilitates more appropriate location of subsequent samples.
- The cost of preparing documents is reduced because only one (or possibly two) work plan(s) and assessment report(s) are necessary.
- The assessment process has less impact on the environment (i.e., it is a greener process) because of the reduced number of mobilizations.

- Remediation of the site can commence sooner, so that constituents of concern (COCs) may not have spread as far from the source, which will limit the area to be remediated.

Disadvantages of dynamic work plans include:

- It may be difficult to estimate the cost of the sampling effort.
- Field sampling equipment may be less precise than fixed-laboratory analysis.
- The responsible professional may be uneasy because the cost of the project is undefined. That is, more or less sampling may be required than originally thought.

## References

California Code of Regulations (CCR) Title 23 (Waters), Division 3. State Water Resources Control Board and Regional Water Quality Control Boards. Chapter 16. Underground Tank Regulations Article 11. Corrective Action Requirements §2722.

California Health & Safety Code, Section 25295.

USEPA. 2001. A Guideline for Dynamic Workplans and Field Analytics. Available at <http://www.epa.gov/swertio1/download/char/dynwkpln.pdf>. Accessed on 24 February 2010.

# Corrective Action Plan

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## Scope of This Chapter

This chapter presents good practices for creating corrective action plans to be used during mitigation measures.

A corrective action plan (CAP) identifies, justifies, and documents the most applicable and cost-effective method of mitigation by:

- Providing a preliminary conceptual design of the corrective action and a description of the tasks necessary to implement the corrective action;
- Obtaining additional data, if necessary, to support the development of detailed design plans and specifications;
- Providing detailed design plans and specifications, including an O&M manual for the corrective-action system and emergency contingency plans in the event of any significant failure of the corrective action system;
- Identifying and obtaining necessary easements and permits required for the implementation of the corrective action; and
- Creating a performance evaluation plan to monitor the effectiveness of the corrective action and to describe corrective action goals.
- Mass to be left in place.
- Set remedial action objectives based on regulatory input.

## CAP Preparation

Preparation of a CAP is predicated on the basis that site assessment is complete to the point that initiating remediation will be cost-effective. Some agencies require the source to be delineated to either some agreed-upon action levels or to non-detectable results before a CAP can be prepared. However, some forms of remediation can be implemented without full delineation and still attain remediation goals.

**Legal.** As defined in the California Code of Regulations (CCR) Title 23, Division 3, Chapter 16, UST Regulations, Article 11, §2725, the RP shall propose a Corrective Action Plan based on the information obtained during the site investigation and with concurrence from regulatory agencies.

CCR Title 23, Division 3, Chapter 16, UST Regulations 2722 (c) states that the responsible party (RP) shall submit the CAP to the regulatory agency for review and concurrence and shall modify the CAP in response to a final regulatory agency directive.

## CAP Implementation

According to CCR Article 11 §2726, the responsibility for implementing the CAP lies with the RP. The RP shall monitor, evaluate, and report the results of implementation of the CAP on a schedule agreed to by the regulatory agency.

Note that the RP may begin cleanup of soil and water before regulatory concurrence if the regulatory agency has not provided a response within 60 calendar days of CAP submittal. In this situation, the RP still must notify the regulatory agency of his/her intention to begin cleanup and comply with any conditions set by the regulatory agency, and shall modify or suspend activities when directed to do so by the regulatory agency. It is recommended that regulatory approval be received prior to beginning work, as this may assist with the overall cost-effectiveness of the corrective action.

**Legal.** Section 2811(a)(5) of the Fund Regulations specifies that corrective-action costs incurred after December 2, 1991, are reimbursable only if the work was done in compliance with applicable corrective action requirements "including the implementing regulations in Article 11, Chapter 16, Division 3, Title 23, California Code of Regulations." The requirement to prepare a CAP before initiating corrective action is described in Article 11.

The regulations in Article 11 are explicit about what the minimum requirements are for a CAP. Different regulatory agencies may have additional requirements, or clarifications, on what they expect a CAP to include.

## Example CAP Contents

The following items are things to be considered when preparing a CAP.

### Introduction

The introduction includes the purpose of the corrective action and the site description, including geologic and hydrogeologic information.

### Summary of Previous Work

The goal of this section is to describe the previous site work, identify the major conclusions of each phase of work, and reference the reports containing the details. This section does not necessarily require a restatement of all of the details of each past report or laboratory results for each sample. The main focus of this section is to include relevant prior data in context with the goals of the CAP. This section may include work performed to date to assess and mitigate the release, evaluation of risk, and feasibility of cleanup methods.

### Justification of Cleanup Goals

It is important to understand the cleanup goals associated with the corrective action to be implemented and to identify the target treatment zone(s). This section should discuss the cleanup goals that the regulator, RP, and consultant determine to be appropriate and achievable.

According to Article 11 §2725, for waters with current or potential beneficial uses for which numerical objectives have been designated in water quality control plans, the RP shall propose at least two alternatives to achieve these numerical objectives. For waters with current or potential beneficial uses for which no numerical objectives have been designated in water quality control plans, the RP shall recommend target cleanup levels for long-term corrective actions to the regulatory agency for concurrence. Target cleanup levels shall be based on the impact assessment.

### Discussion of Corrective Actions

When evaluating potential corrective actions, it is important to compare different technologies to determine which method is the best for site conditions **and** achieves cleanup goals in a reasonable time period with reasonable costs. It is prudent to compare at least three technologies. If these goals cannot be achieved, it is may be appropriate to demonstrate the technical impracticability of implementing cleanup and look to other available methods to mitigate human or environmental risk at the site.

- Include results and data obtained from any treatability or pilot study(ies). These data are the basis for the remedial design and demonstrate the effectiveness of the proposed remediation system(s). Data analysis includes evaluation of suitable corrective actions.
- Provide the anticipated amount of time to achieve the proposed cleanup goals for each proposed corrective action.
- Provide a cost comparison of the various methods. Cost analyses include all aspects of the proposed corrective action (e.g., planning, construction, operation, maintenance, reporting, verification monitoring, disposal, and decommissioning).

### Recommended Corrective Action

The section describes how the best available, most cost-effective remedy is expected to reduce subsurface levels of COCs to cleanup goals. Supporting evidence is needed to justify a high level of confidence that the goals will be met.

System design and plans of the recommended corrective action should include:

- A description of the remediation process and an overview of the equipment required. Remediation design elements may include construction plans (electrical one-line drawings, construction drawings in plan view and/or details, piping or wellhead construction details, remedial well design detail, shoring/grading plans), and other engineering documents.
- A description of the expected pumping rates, treatment efficiencies, etc.
- Certification of the plans by an appropriate registered professional (e.g., a professional certified electrical engineer prepares or stamps electrical one-line drawings).

## Endpoint for Remediation

This section describes the criteria for remediation completion and site closure. It includes a description of how remediation system performance will be documented, and how the progress of the remediation process is monitored. The CAP needs to discuss contingency measures for addressing residual plume components if the proposed method is unsuccessful at meeting the remediation goals,

Part of preparing a CAP is identifying the life-cycle expectations for the remediation process, including appropriate means of documenting progress, and criteria for the remediation endpoint. It is wise for the RPs, consultants, and regulators to agree on the conditions under which the operation of the remediation system will be stopped before initiating active remediation.

## Mass Calculations

Many agencies require an estimate of the total volume or mass of the hydrocarbon-affected soil and/or groundwater to be treated as part of this section. Mass calculations, however, are interpretive, often based on scattered data collected over time, and often cannot incorporate the effects of ongoing natural biodegradation, which may have occurred since the data were collected. Therefore, truly accurate mass calculations are in general difficult to achieve, and mass data may be considered as approximate at best.

## Additional Implementation Details

The following data may be included in the CAP or as part of a subsequent document, as required by the lead regulatory agency.

### Remediation Equipment, Specifications, and/or Materials

This section includes a brief description of equipment specifications or materials to be used during remediation. Appendices can include:

- Manufacturer specification sheets
- Detailed engineering calculations (flow rates, pipe sizes, etc.)
- Copies of design drawings
- Process flow charts

### Waste and/or Materials Management

This section describes any waste or materials-handling requirements associated with the remediation process; for example, management of:

- Granular activated carbon
- Extracted groundwater
- Excavated soil
- Used oil from remediation equipment
- Construction debris from remediation system installation
- Soil cuttings from remediation wells
- Hydrogen peroxide used for advanced oxidation
- Nutrients for bioremediation

### Wells or Other Subsurface Features

This section describes the number and placement of remediation wells necessary for an effective cleanup process or, if a remediation trench is to be installed, a description of its construction and placement.

## Permits and Schedule for Implementation

### Permit Examples

- **Air:** Air Pollution Control District (APCD) Permits (Permit or Authority to Construct or Permit to Operate, or other). Generally, any type of air discharge requires a permit.

- **Water:** Publicly Owned Treatment Works (POTW) (Sewer Discharge) (City or County) or National Pollutant Discharge and Elimination System Permit (NPDES) (Storm Drain Discharge) (Regional Water Quality Control Board).
- **Waste Discharge** (required by some Regional Water Quality Control Boards for injection processes).
- **Well Permits** (obtain from the Public Works Agency, local City or County well ordinance or equivalent – groundwater well permits and groundwater well abandonment permits, boring permits)
- **City or County Building, Electrical, Encroachment, Planning, or Fire Department Permits**
- **Shoring/Grading Permits**

**Note.** It may be more cost-effective for the construction contractor to obtain building/ construction permits than for the consultant to do so. Construction contractors often have significant experience with specific cities' requirements and processes. It can be determined during the bidding process whether the contractor has experience permitting with a specific City or County agency.

### **Schedule**

A schedule should be included with the CAP. The following milestones are examples of things to consider when developing the schedule:

- CAP approval by agency
- Remediation design/plan completion
- Any required Access Agreements for private property
- Emissions or discharge permits
- Construction bid/procurement (consultants or specialty construction contractors, including drillers)
- Building/construction permits
- Any required well or drilling permits
- Construction of remedial technology onsite
- Startup and shakedown and/or baseline sampling
- Transition to routine operation and maintenance (O&M). At this stage, the site transitions from the startup phase to routine operations.
- Estimated time to verify completion of project, remove system, issue NFA letter.

# Reports

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## Scope of This Chapter

This chapter discusses some of the reports needed during the various phases of work at LUFT sites. The specific reports described in this chapter are UST Removal, Site Assessment, Groundwater Assessment, and Case Closure Requests.

A variety of reports are required to present the results of work performed at LUFT sites. These scientific documents are used to determine the direction of the project and to provide verification of the various phases of investigation, assessment, remediation, monitoring, and closure. Reports are used to present information to stakeholders regarding the status of the various phases of work conducted at LUFT sites. The main elements of a technical report are data, data analysis, conclusions, and recommendations.

## Reporting Schedule

Technical reports are to be submitted to the regulatory agency case worker by the assigned due date. If the report cannot be submitted by the assigned due date, the responsible party (RP) or consultant submits a written request for extension, citing the specific reason for the extension request and an anticipated date by which the report can be submitted.

## Reports Approval

The agency case worker reviews reports to determine whether the activities associated with various phases of work at a LUFT site have been conducted and completed as set forth in the approved work plan. The agency is to consider the conclusions and recommendations presented in the report and determine whether further work is required. Based on the agency's assessment, the case worker will provide direction to the RP on how to proceed.

## GeoTracker Reporting Requirements

All reports need to be uploaded to GeoTracker, an on-line tool for submitting data and reports electronically within the State of California; as discussed in the [GeoTracker](#) chapter of this Manual.

# Reports

## Specific Report Types



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This section provides some examples of specific report types that may be required for work performed at a LUFT site. This is not intended to be a complete list of the applicable reports, nor is it intended to list every detail that may be required for each report. It is important the RP/consultant work with the regulatory agency overseeing the case to agree on the expectations for reports and level of detail for the various phases of work at a LUFT site.

### UST Removal Report

A UST Removal Report is generated when a UST is permanently removed from its existing location. The process of removing a tank is discussed in the [Tank Removal and Closure in Place](#) section of this Manual. The report customarily includes the following sections:

#### Signature Page

The removal of a UST needs to be supervised by a registered geologist or engineer. The registered professional must sign off on the provided UST Removal Report.

#### Introduction

Provides background information, including the site description, location of the tank, size, and type of UST, and original date of tank installation. Figures show site location and tank location(s).

#### Description of Removal Activities

- **Permits:** There are different permit requirements, depending on location and agency jurisdiction. This section of the report sets forth how the RP and/or the consultant have complied with the requirements.
- **UST Content Removal and Cleaning:** Describes the procedures employed for cleaning the UST, the quantity of wastewater, and disposal manifest.
- **Excavation:** Includes the dimensions of the excavation required to remove the UST, the condition of soil (odor, staining, visual inspection), and description of the type of soil. If the soil appears to be uncontaminated, provide location of soil stockpile(s) for sampling to determine reusability, if any. Also provides information on over-excavation for areas with contaminated soil.
- **UST and Appurtenance Removal:** Includes date of removal and description of how the tank was rendered inert; also includes oxygen, carbon dioxide, and lower explosive limit (LEL) readings collected in the tank, the excavation, and the breathing zone. A description of the tank condition upon removal, location of tank disposal, and a disposal manifest are also common. It is desired to map the known locations of UST and appurtenance releases if possible.
- **Confirmation Sampling:** Describes where the confirmation samples were collected and summarizes the analytical results
- **Backfill:** This section reports whether the excavated soil is useable for backfill, and includes the analytical results for soil samples to support either a positive or negative verdict on the soil's useability. If "new" fill material is needed, the source and type of soil, as well as the analytical data of the fill, are included. The procedure for backfilling is discussed, and compaction testing is also included. Note: it is highly recommended to obtain regulatory approval to backfill with excavated soil from the tank pit.

#### Conclusions

This section summarizes the activities performed during the UST removal. It also indicates whether further assessment and remediation activities need to occur because of the analytical results obtained during the removal, tank structural failure, and/or other visual observations during the tank-removal process, or whether the tank meets tank-closure criteria. If the UST is determined to be leaking, a LUFT case should be opened up within GeoTracker.



## Site Assessment Report

A Site Assessment Report is prepared to report on the investigative activities performed at and analytical data gathered from a LUFT site. The following items may be included in site assessment reports:

### Presentation of Historical and Recent Site Data

- Site plan with locations of all borings, wells, and other sampling points.
- If previous site assessment data exist, include maps and cross-section(s) showing the soil and bedrock characteristics, and the distribution of contaminants, in both soil and groundwater.
- Table(s) of soil analytical results (in milligrams per kilogram [mg/kg], or as approved by the regulatory agency), with both recent and historical data in chronological order.
- Table(s) of groundwater analytical results (in micrograms per liter [µg/L], or as approved by the regulatory agency), with both recent and historical data in chronological order and tabulated by well number.
- Boring logs and well logs of the most recent site-assessment work.
- Description of the site-specific geology and hydrogeology, updated with the most recent investigative results.
- Revision(s) to the conceptual site model (CSM) which resulted from the current phase of work are presented and discussed in the report text.

### Description of Site Assessment Activities

- Investigative procedures used
- Analytical methods used
- Changes, if any, to the approved scope of work, and rationale for any such changes
- Decontamination procedures
- Waste management (including stockpiles) and disposal procedures
- Stormwater pollution prevention procedures

### Interpretation of Data

It is necessary to interpret the analytical and visual data collected during the investigation to identify source and release areas, delineate the extent of contamination, and establish plans for mitigation. This is accomplished by performing an initial risk screening by comparing the analytical data results gained from the investigation to cleanup levels in order to establish the severity of the contamination. See the chapter on [Risk Evaluation and Risk Management](#) for more details. This section of a site assessment report also includes an estimate of the volume and mass of constituents of concern (COCs) in soil and/or groundwater.

### Conclusions and Recommendations

The technical report presents pertinent conclusions based on the interpretation and analysis of site-specific data by the consultant. The technical report also proposes recommendations for the next phase of work at the site or, if appropriate, presents a request for case closure if the risk screening has indicated that the site poses no risk to human health, safety, or the environment.

All conclusions should be supported, not merely listed. This section should also:

- Discuss whether the work satisfied work-plan objective(s);
- Indicate which case-closure criteria were satisfied; and
- Indicate which significant data gaps remain to satisfy case-closure criteria.

### Groundwater Assessment Report

The California Board of Geology and Geophysicists provides guidelines for groundwater investigation reports: <http://www.geology.ca.gov/forms-pubs/groundwater.pdf>

## Reporting of Monitoring Results

**Legal.** Per SWRCB Resolution No. 2009-0042, semiannual or less frequent monitoring is sufficient at LUFT sites. If more than semiannual monitoring is required for a case, the RP and SWRCB shall be notified of the rationale by the lead regulatory agency, and the notice shall be posted on GeoTracker.

Periodic monitoring is required to examine the performance of the remedial system(s) installed at LUFT sites. A report is submitted to the regulatory agency in a timely fashion after each semiannual monitoring event. The monitoring report includes information on system status and operation, monitoring records, and progress evaluation, including volumes treated and amount of hydrocarbons removed. Any changes, modifications, or other significant information which may affect the remedial design are also reported. The frequency of monitoring and reporting intervals may change based on direction from the lead regulatory agency.

### Case Closure Request Report

When the RP has performed the stages of work required by the lead regulatory to ensure that the site poses no significant risk to human health or the environment, the RP or his/her consultant prepares a technical report justifying the case-closure request. Often with a Case Closure Request, a risk assessment has been performed and the RP and regulator agree that the site poses no significant risk to human health and is ready for closure despite the presence of residual contamination.

The request summarizes the work that has been performed to date and demonstrates how the work satisfies the following criteria established by the Regional Water Quality Control Board (RWQCB), which are:

- The release has been stopped and ongoing sources of COCs have been removed or remediated,
- The site has been adequately characterized,
- The COCs are not migrating,
- No water wells, drinking-water aquifers, surface water, or receptors are likely to be impacted, and
- The COCs pose no significant risk to human health, safety, or the environment and will degrade to water quality objectives (WQOs) within a reasonable amount of time.

The following sections comprise information that may be included in a Case Closure Request Report. Much of the content of the Report can likely be obtained from previous site reports, obviating the need to “re-invent the wheel.”

#### Extent and Stability of COCs

This section presents the lateral and vertical extent of contamination at a LUFT site. While all of the following components may not apply to a particular site, and hence not require discussion (e.g., if NAPL has never been observed at the site, then the extent of NAPL need not be discussed), justification is generally expected to be provided when omitting components which might, to other stakeholders, appear applicable. All conclusions regarding the adequacy of assessment and the stability of the contamination must be justified.

- Lateral and vertical extent of NAPL
- Lateral and vertical extent of the COCs in unsaturated-zone soil
- Lateral and vertical extent of COCs in saturated-zone soil and the smear zone
- Lateral and vertical extent of the COCs in groundwater
- Lateral and vertical extent of the COCs in subsurface vapor
- Discussion of the stability of the associated plume. For example, the groundwater plume is stable in position and is showing declining levels.

#### Effectiveness of Remedial Actions

This section identifies the approved cleanup levels, the areas and media targeted by the remediation, the type of remediation used, the period of time over which various remedial options have been implemented, and the effectiveness of the remedial action(s) in reducing the concentrations of COCs and meeting remedial objectives. System operation and maintenance (O&M) data and monitoring and verification sampling data are presented to substantiate the conclusions presented in this section.

### **Impact of Residual COCs on Public Health/ Environment**

This section demonstrates that the contamination does not pose a significant risk to human health, safety, or the environment, and that residual groundwater contamination will attenuate within a reasonable time frame. The report demonstrates that receptors are not, and will not be, adversely impacted and that potential exposure pathways are not complete to a level which might pose a significant risk to human health or the environment. See [Risk Evaluation and Risk Management](#) chapter for further details.

### **References**

State of California State and Consumer Services Agency. 1998. The California Board of Geology and Geo-physicists. Guidelines for Groundwater Investigation Reports. <http://www.geology.ca.gov/forms-pubs/groundwater.pdf>. July 1998.

# Green and Environmentally Responsible Cleanups

Version 1.0 - Draft August 2010



## Scope of This Chapter

The use of environmentally responsible, or “green,” strategies to remediate contaminated LUFT sites is encouraged. Although a cleanup already promotes environmental responsibility by removing health threats and restoring contaminated land and water to beneficial uses, additional sustainability benefits can be achieved that will balance and maximize both short- and long-term environmental benefits to the local and global communities. This chapter is intended to provide a brief, general framework for using strategies, practices, and technologies that reduce the environmental footprint of LUFT cleanups.

First and foremost, the State Water Resources Control Board (SWRCB) is concerned with meeting all the statutory and regulatory requirements for LUFT cleanups. Environmentally responsible strategies can be integrated into cleanup actions using a range of practices and technologies, as set forth in this chapter, in the associated reference documentation, and in standard guides.

Environmentally responsible cleanups should seek opportunities to optimize and encourage innovations related to, but not limited to, the following areas:

- Reducing energy use
- Reducing generation of air pollution and greenhouse gas emissions
- Reducing water use and impacts to water resources
- Considering land use and protection of ecosystems
- When generating waste: Reduce, Reuse, and Recycle material and waste

If the criteria listed above are going to be applied to a site, options should be considered for all stages of the cleanup process, including site assessment, system design and installation, system operation, and site-closure activities. The scope of applicability of green options can vary from considering the direct impacts of on-site activities and transportation to performing a life-cycle analysis of the cleanup. However, due to the relatively small size of LUFT sites and fairly uniform remediation options, the most efficient way to proceed is usually towards a quick and simple analysis which, at a minimum, considers direct impacts to the environment and impacts from transportation.

Quantitative calculators or life-cycle analysis tools can be used to properly apply measures during remediation to maximize environmental sustainability benefits. These tools can help account for the manufacture, use, and transport of materials, products, equipment, and wastes associated with all phases of a cleanup. They may allow for quick and easy identification of activities with the most significant impact. Their results can illuminate ways to reduce environmental impact with minor to moderate changes.

## Practices, Strategies, and Technologies to Support Environmentally Responsible Cleanups

### Energy Use

- Minimize energy consumption (e.g., use energy-efficient equipment)
- Power cleanup equipment through on-site renewable energy sources
- Purchase commercial energy from renewable resources

### Air Toxics and Greenhouse Gas Emissions

- Minimize use of heavy equipment
- Maximize use of machinery equipped with advanced emission controls
- Use cleaner fuels to power machinery and equipment
- Sequester carbon dioxide onsite (e.g., soil amendments, re-vegetation)
- Minimize dust generation and airborne transport of contaminants
- Minimize number of trips to the site and number of vehicles required for cleanup.

**Water Use and Impacts to Water Resources**

- Minimize water use and depletion of natural water resources
- Capture both clean and treated water for reuse (e.g., aquifer recharge, irrigation, consumption)
- Minimize water demand for re-vegetation (e.g., native species)
- Employ best management practices for stormwater

**Land Use and Protection of Ecosystems**

- Integrate anticipated site use or reuse plans into the cleanup strategy
- Minimize areas requiring activity or use limitations (e.g., destroy or remove contaminant sources)
- Minimize unnecessary soil and habitat disturbance or destruction
- Restore or create habitat using native species and local materials (e.g., rock)
- Minimize noise and lighting disturbance

**Waste Management: Reduce, Reuse, and Recycle Material and Waste**

- Minimize consumption of virgin materials
- Minimize waste generation
- Use recycled products
- Segregate and reuse or recycle materials

**References**

California Department of Toxic Substances and Control (DTSC). 2009. Interim Advisory for Green Remediation.

U.S. EPA Office of Solid Waste and Emergency Response (OSWER). 2009. Principles for Greener Cleanups.

U.S. EPA Region 9. 2009. Greener Cleanups Policy.

## **CALIFORNIA LUFT MANUAL**

### **SECTION 2: INITIAL RESPONSE, REPORTING, AND TANK REMOVAL**

# Initial Reporting and Abatement

Version 1.0 - Draft August 2010



## Scope of This Chapter

Federal and State agencies require owners and operators to respond to a confirmed unauthorized release from an UST. The benefit of this chapter is to provide owners and operators a guide on how to identify and confirm a release and determine what steps to take as an immediate response to stop further impact to the surrounding environment.

An unauthorized release, as defined by California Health and Safety Code (H&SC) §25295, is a release which escapes from a UST's secondary containment, or from the primary containment, if no secondary containment exists, increases the hazard of fire or explosion, or causes any deterioration of the secondary containment of the underground tank system.

An unauthorized release can happen at any moment—during tank fueling or by failure of a tank wall. Regardless, it is the responsibility of the owner or operator to respond and report the release to state and/or federal agencies.

## Initial Response

Once an unauthorized release is detected, the owner or operator has 24 hours to report the discovery. The release may be reported via telephone or electronic mail to the lead regulatory agency. The lead agency is determined based on the quantity of the spill and the impacted media. The RP should first report to the agency that has issued permits at the affected site, usually the Local Implementing Agency (LIA) or the Local Oversight Program (LOP), to determine whether one of them has jurisdiction over the release. If the LIA or LOP does not have jurisdiction, the case will fall under the jurisdiction of the Regional Board.

The next step is to take immediate action to stop the leak and prevent further release. This may require removing the residual product from the equipment in question. It is critical to determine whether or not any fire, explosion, or vapor hazards are present and, if so, to mitigate them.

## Reporting

An Unauthorized Release Report needs to be submitted to the lead regulatory agency within five days of the release confirmation. The report should include, but is not limited to, the following:

- The operator's name and telephone number;
- A list of the types, quantities, and concentrations of hazardous substances released;
- A description of the actions taken to control and clean up the release;
- The method and location of the disposal of the tank and additional removed items such as product piping, excavated soils, etc., if applicable.
- Description of actions taken to repair the UST and to prevent future releases;
- Description of the method used to reactivate the interstitial monitoring system after replacing or repairing the primary containment; and
- The integrity of the secondary containment.
- Description of possible fire, explosion, or vapor hazard.

The lead agency may request that the RP conduct an initial site characterization to quickly determine how the release may have occurred and its estimated quantity.

## Initial Abatement Actions

Unless otherwise directed by the lead agency, owners and operators are required to perform these initial abatement measures in response to an unauthorized release:

- Remove as much of the substance from the UST system as possible to prevent further impact to the environment;
- Visually inspect for substance release above- or below-ground and attempt to prevent further substance migration into the surrounding soils and groundwater;

- Continue to identify, monitor, and mitigate any additional fire and safety hazards posed by potentially migrating vapors or free product from the UST excavation zone.

## References

California Code of Regulations, Title 23, Division 3, Chapter 16, Article 5.

California Health & Safety Code, Sections 25291, 25292, 25294, and 25295.

40 Code of Federal Regulations, Subtitle F.

U.S. EPA, Office of Environmental Guidance, RCRA Subtitle I.



# Release Response Prioritization

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## Scope of This Chapter

This chapter discusses the various types of responses that occur as a result of an unauthorized release. The threat to human health, safety, and the environment will determine whether an urgent, interim, or long-term response is appropriate.

### Urgent Response

“Urgent response” includes scenarios where imminent threat to human health or the environment results from sudden and/or large releases of fuel products, such as a tanker truck or rail car overturning. Because this Manual addresses issues pertaining to leaking *underground* fuel tanks (LUFTs), the most likely urgent-response scenario is a tank breach/failure or a major line loss. Evidence for this event could include light non-aqueous phase liquid (LNAPL) surfacing or appearing in storm or sanitary sewers or utility conduits, loss of inventory, strong odors/vapors, explosions, or fires.

Remediation in these instances will consist first of emergency response actions, such as immediate containment and recovery of spilled fuels, often in cooperation with local Hazardous Material agencies, fire departments, etc. Remediation of residual impacts after public safety has been protected will then take place following standard procedures for non-urgent response remedial actions.

### Rapid Response/Interim Remediation

Interim remediation may be approved by the local regulatory agency in cases where the risk to human health, safety, and/or the environment may be less than in an urgent-response scenario, but sufficient to warrant rapid actions; for example, to contain a migrating groundwater plume or expanding LNAPL footprint.

Interim remediation may be pursued as approved by the regulator concurrently with other required site actions, such as lateral plume delineation or bench testing for a final remedy.

Interim remediation does not necessarily supersede the requirement for a formal analysis of final remedies, including submittal of a Corrective Action Plan (CAP). The regulatory case worker may, however, allow interim remediation to stand as the final remedy if it can be demonstrated that remedial goals are being met; for example, that the groundwater plume is stable in position and is showing declining levels. Proposals for initiation and/or continuance of interim remediation usually take the form of work plans.

Updates on the progress of interim remediation should be included in routine reports, or as otherwise approved by the regulatory agent. For example, a work plan may contain a proposal to conduct interim remediation for six months, followed by a report of findings with recommendations for additional site actions. Check with the lead regulatory agency for the required reporting documentation, outline, and format.

Examples of interim remediation processes include (but are not limited to):

- Mobile (non-fixed) or temporary treatment systems and processes.
- One-time oxidant or bio-augmentation material injection events.
- Periodic or extended single-event batch extractions.

Rapid response is used where health/environmental risk drivers (e.g., an immediate need for plume containment) or other drivers (e.g., property redevelopment) affect remedial method selection. Examples of rapid-response remediation processes include (but are not limited to) remedial excavation and sustained-batch extraction.

Remedial excavation is effective as a means of removing impacted soils rapidly but, in many instances, is ineffective at addressing groundwater issues, unless a groundwater plume is localized or derives primarily from low-permeability soils.

Sites with widespread groundwater issues may not significantly benefit from remedial over-excavation. In general, remedial excavation is less cost-effective compared with other remediation processes, except in heavy clay soils with shallow groundwater conditions. Sites like these are often resistant to other forms of remediation.

## Longer-Term Response

If interim remediation is unsuccessful or not implemented, longer-term remediation may be pursued. Longer-term remedial processes are pursued after submittal of a Corrective Action/Remedial Action Plan to the lead regulatory agency for approval.

Longer-term response actions often involve fixed remediation equipment connected to public utility lines (natural gas, electricity, sewer, and/or storm drains). Local city/county permits may be required to install the remediation equipment enclosure, subsurface piping, aboveground remediation equipment, and remediation wells. Discharge permits may be required by local air districts, water districts, or State/County/local agencies. Installation of a fixed remediation system normally requires professional engineering and construction contractor planning, design, and oversight. Construction should be completed using a licensed, appropriately trained, and certified contractor.

Construction of fixed remediation systems usually includes installation of underground conveyance piping. Active property use presents challenges to piping installation, as piping must be routed around existing site features but at the same time must connect to treatment wells installed in the target site areas (such as the areas of highest concentrations). Business or occupant/community disruption is unavoidable during construction and should be weighed with other factors when selecting a remediation process.

Examples of longer-term remediation processes include (but are not limited to):

- Soil-vapor extraction (SVE) systems
- Bioventing
- Bio and air sparging
- Groundwater-extraction systems

See the [Remediation](#) chapter for further discussion.

# Tank Removal and Closure in Place

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## Scope of This Chapter

This chapter provides suggestions on how to prepare for removal of an UST or how to properly close it in place.

## UST Removal or Closure in Place

There are two methods to properly decommission a UST. The first is to completely remove the UST, and the second is to fill it with an inert solid and leave it in place.

If a leak is confirmed and cannot be repaired, it is recommended that the UST and/or piping be removed, depending on the evidence of leakage and specific site features. Most responsible parties (RPs) elect to remove the UST, and this is the method generally preferred by regulatory agencies.

Closure in place is recommended only in cases in which undue damage to nearby utilities or building foundations is of concern, or when regulatory agencies do not approve of UST removal. Closure in place is generally not recommended due to the possibility of overlooking contamination or complicating future development at the site.

There are several steps that need to be taken in order to remove or close a UST in place, including field work preparations, UST removal, confirmation sampling, free-product removal from the soil (if necessary), and reporting.

## Pre-Field Work Considerations

There are several things to consider prior to the actual removal of a UST, including obtaining the proper permits, locating the UST and the associated infrastructure (all piping and appurtenances), and ensuring that underground and overhead utilities have been properly located. The Pre-Field Work Considerations section of the [Site Assessment](#) chapter is a good source of points to consider prior to mobilizing for field work.

## Permitting

Permitting for tank removal varies from site to site and from agency to agency. Generally, Local Implementing Agencies (LIAs) and Local Oversight Program (LOP) agencies have jurisdiction over UST removals and will provide direction on the required permits.

## Health and Safety

Health and safety are always of importance when conducting field work and are paramount due to the nature of working with fuel; limited oxygen, toxic gas, and fire and explosion hazards are of real concern. A plan for managing the risk should be considered prior to entering the field. The Health and Safety chapter provides guidance on safety considerations and on preparing [Health and Safety Plans](#).

## Mitigate Fire/Explosion Hazard

The first step is always to mitigate any fire or explosion hazard. If the material that was stored in the UST was flammable and conditions onsite represent a fire or explosion hazard at "standard temperature and pressure," the UST should be rendered inert using an inert gas such as nitrogen or carbon dioxide ("dry ice"). This reduces the oxygen content of the "ullage" (the space above the fuel that contains air and fuel vapors) to below the combustion threshold. Without sufficient oxygen in the tank, the fuel vapors in the ullage cannot ignite, and an explosion does not occur.

## Tank Decontamination

Decontamination of all liquid, solid, and sludge from the UST and associated piping is necessary before the tank is removed or closed in place. The waste must be properly disposed of by a licensed waste hauler, and waste manifests must be received from the disposal facility.

**Important!** It is important that a combustible gas indicator (CGI) be used during all field work to ensure worker safety.

## Tank Removal

If the tank is to be removed, the UST and associated piping should be unburied using excavation equipment. It is important to avoid using sparking tools during removal activities, as explosive conditions may be present. It is also important to avoid ignition sources such as static electricity, flames, and smoking.

Site inspection by local agencies is generally required and typically takes place after the UST and its associated piping are fully exposed. It is the responsibility of the RP to inform the regulatory agency in advance of the removal activities.

A tank is typically removed using a small crane and associated heavy machinery or by other means after any explosion hazard has been mitigated by rendering the tank inert using dry ice or other means. Generally, a tank-removal contractor with prior experience is hired to ensure successful and safe removal.

The tank itself should be treated as contaminated regardless of whether it is to be recycled or disposed (CCR Title 23, Division 3, Chapter 16, Article 7). Regulations vary from jurisdiction to jurisdiction regarding dismantling a UST onsite. In general, a treatment, storage, and disposal (TSD) facility should be used to dismantle, dispose of, and/or recycle a contaminated UST. It is important to contact the lead regulatory agency regarding disposal and recycling options for the specific jurisdiction for the site.

If standing water is encountered in the excavation, a grab sample should be collected and analyzed for proper disposal characterization. After the water sample has been collected, it is recommended that the excavation be pumped dry, if possible, and retained in appropriate containers for disposal.

Soil samples must be collected to confirm the presence or absence of an unauthorized release. See the Confirmation Sampling section below for further details.

## Closure in Place

It is important to determine whether an unauthorized release has occurred prior to closing a tank in place. The Confirmation Sampling section below discusses the procedures for collecting confirmation samples.

Upon confirmation that an unauthorized release has not occurred and after regulatory approval has been received, the tank can be filled with an inert material. A regulatory agency representative is usually required to witness the filling of the tank with inert material.

If an unauthorized release has occurred, additional characterization and remedial action will be necessary prior to closing the tank in place.

## Confirmation Sampling

When a UST is removed or closed in place, California H&SC Division 20, Chapter 6.7, Section 25298 requires the UST owner/operator to “demonstrate to the local agency that there has been no significant soil contamination resulting from a discharge in the area surrounding the UST or facility.” This is referred to as confirmation sampling.

Generally, a regulatory agency representative will be present during tank removal/closure in place to ensure that the proper response actions are implemented if free product or contamination is encountered.

Sampling procedures should be conducted in accordance with guidance provided from the lead regulatory agency.

## Sampling for Tank Removal

Confirmation samples are collected from potential worst-case locations, including:

- Below the tank invert
- Below the product line
- Below the tank piping
- From stockpiled soil that has been removed from the excavation

The best place to collect soil samples is from the bottom of the excavation, as opposed to next to the excavation. At some sites, it may be safe to enter the excavation. In these situations, samples will likely be collected with a corer or trowel. However, in most cases, samples can only be safely obtained from a backhoe bucket. Commercial or custom-made hand-corer extensions can be used to collect samples from minimally disturbed soil.

Soil samples should be collected where visual staining or discoloration is observed or where the vapor monitoring instrument indicates the highest readings.

To sample below the tank invert, collect samples 2 to 4 feet into native soil.

- For tank volumes less than 12,000 gallons—collect one soil sample at each end of the removed tank (two samples total)
- For tank volumes greater than 12,000 gallons—collect one soil sample at each end of the removed tank and one sample below the center of the removed tank (three samples total)

To sample below the product lines, collect soil samples at 2 to 4 feet vertically and at 20-foot intervals linearly. Include one additional sample at each dispenser.

When collecting confirmation samples for tank piping, soil samples should be collected between 2 and 4 feet below the piping; if possible, choose a sampling location near the joint connector.

At the soil stockpile, retrieve one sample per 100 cubic yards of soil linearly and between 2 and 4 feet below the surface of the stockpile. Samples collected from the excavated soil will indicate whether the soil should be disposed of as a hazardous waste or if it can be reused.

If standing water is encountered in the excavation, it is necessary to characterize the water to determine whether it will need to be disposed of as a hazardous waste. It is recommended that a grab sample be collected and submitted for laboratory analysis.

All samples should be analyzed for applicable constituents of concern (COCs) using approved methods. See the chapter on [Laboratory Analysis and Methods: Soil and Groundwater](#).

### Sampling for Tank Closure in Place

The sample-collection approach for a tank closure in place is different from the approach used for confirmation sampling for tank removal.

Test borings should be installed at an angle so that their tip is below the center of the tank. If an angled test boring is not possible, the RP is required to document and provide an explanation.

For single tanks (separated from other tanks by at least 20 feet), at least two soil borings should be installed, one at each end of the tank, along the tank's major axis.

Soil borings for multiple tanks should be placed along a 20-foot interval around a tank cluster (tanks less than 20 feet apart). Please note that this may change, based on actual site conditions. Soil samples are generally collected from the boring locations at 5, 10, 20, 30, and 40 feet below ground surface (bgs), until evidence of contamination is no longer present.

Samples should be analyzed for applicable COCs using approved methods. See the chapter on Laboratory [Analysis and Methods for Soil and Groundwater](#).

### Free Product or Contamination Removal

Free product and/or contamination can be detected by visual observation (i.e., Light Non-Aqueous Phase Liquid [LNAPL] on the water surface), by the use of a photo-ionization device (PID), or by analytical methods. Samples sent to laboratories should be analyzed for contaminants appropriate to the material stored in the UST.

If the presence of free product and/or contamination is confirmed, removal activities may be necessary if levels exceed those designated by the lead agency. "Free product shall be removed in a manner that minimizes the spread of contamination into previously uncontaminated zones by using recovery and disposal techniques appropriate to the hydrogeologic conditions at the site" (CCR Title 23, Division 3, Chapter 16, Article 5, Section 2655). Removal should be conducted in accordance with the lead agency's guidance and local regulations, and in a manner that minimizes fire/explosion hazard. Removed product and contaminated soil should be treated as hazardous materials (CCR Title 23, Division 3, Chapter 16, Article 7).

Refer to the [Soil Excavation](#) section of the Remediation chapter for further guidance on proper excavation activities.

**Important!** A free-product-removal report must be filed with the SWRCB within 45 calendar days of the initial release report.

If free product is encountered and a removal action is necessary, a proper report is required. Per CCR Title 23, Division 3, Chapter 16, Article 7, Section 2655, the report should include the following:

- Name of person(s) responsible for the removal of the free product
- The quantity, type, and thickness of the free-product layer discovered in the excavation
- How the free product was removed from the subsurface
- Whether any discharge will take place onsite or off-site during the recovery operation, where it will take place, treatment applied to it (if applicable), and the quantity of the effluent of this discharge
- The means of disposal of the free product

**Legal.** The following regulations govern tank-removal activities in the State of California:

- Health & Safety Code (H&SC), Section 25295
- California Code of Regulations (CCR), Title 23, Division 3, Chapter 16, Articles 5, 7, and 11

## References

California Code of Regulations, Title 23, Division 3, Chapter 16, Articles 5, 7, and 11.

California Health & Safety Code, Section 25295.

County of Orange Environmental Health Department. 2005. Guidelines for the Removal of an Underground Storage Tank. February 10.

County of San Diego. 2004. Site Assessment and Mitigation (SAM) Manual, Section 2: Underground Tank Program. February 18, 2004, revised 2009.

State of California. 1989. Leaking Underground Fuel Tank (LUFT) Task Force. *LUFT Field Manual*. Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. October.

# **CALIFORNIA LUFT MANUAL**

## **SECTION 3: INVESTIGATION AND REMEDIATION**

# Fate and Transport of Petroleum in the Subsurface

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## Scope of This Chapter

This chapter presents the fate and transport of petroleum fuels and their individual constituents in the subsurface. This chapter will discuss the various types of fuels, the chemical composition of those fuels, and how the different petroleum constituents behave in the subsurface. This chapter will not provide detailed background on hydrogeology.

The most important thing to understand about the fate and transport of a petroleum release is that petroleum enters the subsurface as an immiscible fluid which is a mixture of thousands of constituents. Its immiscible property is similar to that of other releases, but the fact that petroleum is a *mixture* of constituents is unique and affects the fate of those constituents in the subsurface.

## Generalized Chemistry of Petroleum and Refined Petroleum Products

### Petroleum Chemistry

Crude oil and refined petroleum products are primarily composed of molecules containing only carbon and hydrogen atoms (hydrocarbons). These hydrocarbon molecules are divided into two classes:

- Aliphatic compounds and
- Aromatic compounds

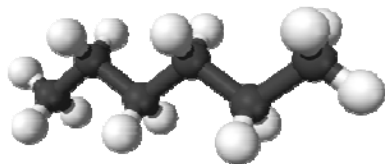
### Aliphatic Compounds

In aliphatic compounds, carbon atoms are joined together in straight chains (normal), branched chains (iso), or non-aromatic rings (cyclic). They are joined by single bonds (alkanes), double bonds (alkenes), or triple bonds (alkynes). However, they do not contain ring compounds with double bonds. In the general scientific literature, alternate terms may be used for these compounds. Alkanes are sometimes referred to as paraffins, and alkenes may be called olefins.

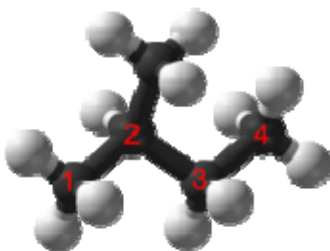
Alkenes, which occur only in refined petroleum products, have carbon-carbon double bonds, with structures that are normal or branched (Zemo and Foote 2003).

The simplest hydrocarbon molecule is methane ( $\text{CH}_4$ ), which has one carbon atom (C) surrounded by four hydrogen atoms (H). Next is ethane, which contains two C's and six H's. Examples of aliphatics are shown below, with the specific compound name in parentheses.

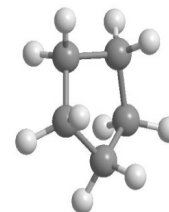
Normal Alkane (n-Hexane):



Branched Alkane (2-Methyl Butane):



Cycloalkane (Cyclopentane):

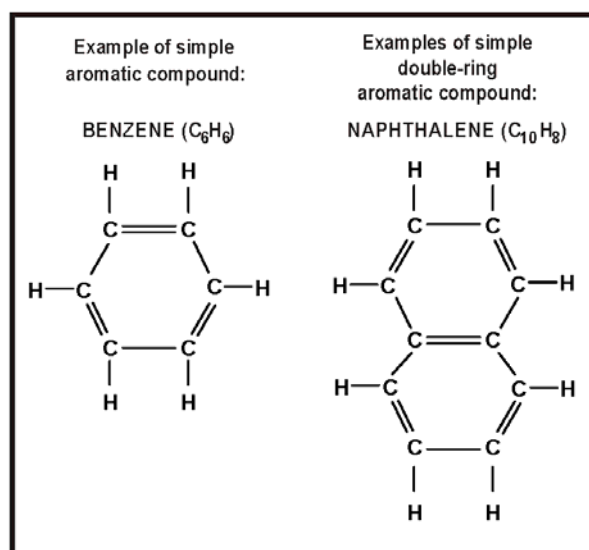


### Aromatic Compounds

Aromatic compounds, or aromatics, are unsaturated ring-type (cyclic) compounds (i.e., the ring contains a double bond), and can contain a single ring (monoaromatic) or multiple rings (polycyclic-aromatic). Aromatic structures are made of carbon rings that are deficient in hydrogen. All aromatics have at least one benzene ring (a single-ring compound characterized by three double bonds alternating with three single bonds between six carbon atoms) as part of their molecular structure (see illustration).



Benzene is the smallest single-ring aromatic compound; naphthalene is the smallest multi-ring aromatic, with two fused rings as shown below.



## Heterocyclic Compounds

Crude oil and some petroleum products (diesel and heavier) can contain molecules that include nitrogen (N), sulfur (S), and oxygen (O) in their structure; these compounds are often referred to collectively as NSOs. These molecules, called “heterocyclics,” are ring compounds where at least one of the compounds in the ring is not carbon; that is they are *not* hydrocarbons. The amount of heterocyclics present in products varies widely, usually in correlation with higher molecular weight.

## Composition of Petroleum Products

Crude oil, which contains molecules with the widest range of sizes (e.g., from 2 carbons to more than 40 carbons; C2 to C40+) is refined into petroleum products ranging from gasoline to asphalt. These refined products are composed of hundreds to thousands of aliphatic and aromatic compounds. The products are refined to meet specifications for either performance in engines (fuels) or specialty products (e.g., lubricating oils, cutting oils, etc.). Additives and blending agents are often added to fuels to improve performance and stability.

Typical products stored in USTs include:

- Gasoline
- Middle distillates (including diesel and other fuel oils)
- Lubricating oils

### Gasoline

Gasoline is a very complex mixture; it is typically composed of C4 to C12 hydrocarbons (that is, hydrocarbons comprising 4 to 12 carbon atoms), with the majority of the mass between C4 and C10. These lighter-weight hydrocarbons include aliphatics and the monoaromatics (including benzene, toluene, ethylbenzene, and xylenes [BTEX] and the alkylated benzenes like the trimethylbenzenes). Minor amounts of the smallest polycyclic aromatic hydrocarbons (PAHs), naphthalene and methylnaphthalenes, are also usually present. The proportion of various hydrocarbons present is variable and is a function of the refining process and performance specifications. Gasoline also contains additives or blending agents whose constituents and relative volume have changed over time due to performance criteria and regulatory requirements. These additives/ blending agents include:

- 1) For leaded automotive gasoline (not sold in California since 1992), the alkylated organic lead species:
  - a. tetra methyl lead (TML),
  - b. tetra ethyl lead (TEL) and related compounds, and

- c. the associated lead scavengers (ethylene dichloride [EDC] or 1,2-dichloroethane [1,2-DCA], and ethylene dibromide [EDB]).
- 2) For recent and current automotive gasolines, the oxygenates, such as:
- a. methyl tert butyl ether (MTBE, banned in California since 2004),
  - b. ethyl tert butyl ether (ETBE),
  - c. tert amyl methyl ether (TAME),
  - d. di-isopropyl ether (DIPE), and
  - e. alcohols, such as t-butyl alcohol (TBA) and ethanol (EtOH).

Research has shown that organic lead species are not typically persistent in the environment unless liquid-phase product is present (Mulroy and Ou 1998).

Other sources of information regarding gasoline composition and its changes since the 1920s are provided in the [References](#) at the end of this chapter.

### ***Middle Distillates - Diesel and Other Fuel Oils***

Diesel fuel and fuel oils are much less chemically complex than gasoline, and their components have not changed very much throughout refining history. Fresh diesel fuel #2 (also called fuel oil #2) is composed primarily of C10 to C25 hydrocarbons, which themselves consist largely of aliphatics, with minor amounts of monoaromatics and PAHs, especially naphthalene and the methylnaphthalenes (EPA 1996). The larger PAHs are generally not found in diesel #2, but can be present in the heavier fuel oils. Fresh fuel oils are abundant in *n*-alkanes but, after weathering, they are dominated by branched and cyclo-alkanes. Other middle-distillate fuels include:

- Kerosene (approximately C8 to C18),
- Kerosene-based jet fuels (e.g., Jet A or JP-5 [C8 to C18] or JP-8 [C8 to C20]),
- Diesel fuel #1 or fuel oil #1 (approximately C8 to C22),
- Heavier fuel oils such as marine diesel or diesel/ fuel oil #4 (approximately C12 to C30).

Bunker fuel (approximately C12 to C35+), also called fuel oil #6 or Bunker C, is the heaviest fuel, and is typically classified as a residual oil. Bunker fuel is very viscous and is frequently “cut” or blended with a diesel-range oil to improve its flow properties.

Because of their larger molecular sizes, middle-distillate fuels tend to be denser, much less volatile, and much less soluble than gasolines. Small aromatics (including BTEX) are generally found only in trace amounts in middle-distillate fuels.

Fuel oils also contain heterocyclic molecules (NSOs) inherited from the crude oil. The typical percent of NSOs increases in heavier fuels: diesel ranges from 1 to 5% NSOs, and fuel oil #6 ranges from 30 to 50% NSOs. The regulatory limits regarding acceptable amounts of sulfur in diesel fuel have changed over time.

### ***Lubricating Oils (Including Waste Oils) and Hydraulic Oils***

Lubricating oils are composed primarily of C25 to C32 hydrocarbons, which are almost exclusively aliphatics (branched and cyclic alkanes). Aromatic hydrocarbons are not present in lubricating oils prior to their use in engines. Because of their very large molecular sizes and the fact that they are almost exclusively aliphatic, unused lubricating oils are nearly insoluble in groundwater and are not volatile.

However, when lubricating oils are used in engines, they pick up fuel components due to cross-leakage in the chambers and often acquire trace concentrations of metals from engine wear (“wear metals”). Used lubricating oils can, therefore, contain aromatics, smaller hydrocarbons, and wear metals.

Hydraulic oils were permanently exempted from regulation by the California State Water Resources Control Board (SWRCB) in January 1996 due to the technical finding that these base oils present very little risk to human health or groundwater quality (SWRCB letter, 11/14/95; SWRCB “Report on Hydraulic Lift Tanks,” February 1995).

## **Physical/Chemical Properties of Petroleum Products and Individual Constituents**

A number of properties, including density, viscosity, solubility, and vapor pressure, can affect the mobility and partitioning of liquid-phase petroleum in the subsurface. Thus, the properties of the compounds are also extremely important for evaluation of appropriate remedial technologies. A compilation of these properties for selected petroleum constituents, products, and crude oils is provided in Table 1 below. In general, as the average molecular size and weight of a product increase, the density increases, the viscosity increases, and the ability of the product to move through the subsurface

materials *decreases*. The following table provides densities and viscosities for water and various crude oils and petroleum hydrocarbon products.

Table 1 – Representative Properties of Selected LNAPLs and Constituents

Chemical	Molecular Weight (g/mol)	Density <sup>(1)</sup> (g/cm <sup>3</sup> )	Dynamic Viscosity <sup>(1)</sup> (cp)	Pure-Compound Water Solubility <sup>(1)</sup> (mg/L)	Pure-Compound Vapor Pressure <sup>(1)</sup> (mm Hg)	Henry's Law Constant <sup>(2)</sup> [(mg/m <sup>3</sup> )/(mg/L)]
Benzene	78.1	0.8765	0.6468	1.78 E+03	76	0.23
Ethylbenzene	106.2	0.867	0.6468	1.52 E+02	7	0.32
Toluene	92.1	0.8669	0.58	5.15 E+02	22	0.27
m-Xylene	106.2	0.8642 <sup>(2)</sup>	0.608	2 E+02	9	0.29
o-Xylene	106.2	0.880 <sup>(2)</sup>	0.802	1.7 E+02	7	0.21
p-Xylene	106.2	0.861 <sup>(2)</sup>	0.635	1.98 E+02 <sup>(2)</sup>	9	0.28
2,2,4-Trimethylpentane	114.2	0.688 <sup>(2)</sup>		2.4 E+00 <sup>(2)</sup>	49 <sup>(2)</sup>	125
MTBE	88.15	0.74 <sup>(2)</sup>	---	5 E+04 <sup>(2)</sup>	251 <sup>(2)</sup>	0.024
Water	18.0	0.998 <sup>(3)</sup>	1.14 <sup>(3)</sup>	---	---	---
<b>Common Petroleum Products</b>						
Automotive Gasoline	100-105	0.72 – 0.76 <sup>(4)</sup>	0.63 <sup>(3)</sup>	---	---	---
Jet Fuel (JP-4)	165(USEPA on-line)	~0.75	~0.83	---	---	---
Kerosene	170 (OSHA)	0.84 <sup>(3)</sup>	2.30 <sup>(3)</sup>	---	---	---
#2 Diesel	233(USEPA on-line)	0.83 – 0.87 <sup>(3)</sup>	2.70 <sup>(3)</sup>	---	---	---
#6 Fuel Oil	>250 <sup>(5)</sup>	0.87 – 0.95	14.5 – 493.5 <sup>(4)</sup>	---	---	---
Crankcase Oil	>250 <sup>(5)</sup>	0.84 – 0.96 <sup>(3)</sup>	~275 <sup>(4)</sup>	---	---	---
Alberta Crude Oil	>300 <sup>(5)</sup>	0.84 <sup>(3)</sup>	6.43 <sup>(3)</sup>	---	---	---
Prudhoe Bay Crude Oil	>300 <sup>(5)</sup>	0.91 <sup>(3)</sup>	68.4 <sup>(3)</sup>	---	---	---

Sources: API 1996; USEPA 1990; Lyman and Noonan 1990; Moyer 2003, USEPA Regional Screening Levels (RSLs) (chemical properties sheet downloaded June 2010.)

Notes:

- (1) Values are given at 20°C unless noted.
- (2) Value is at 25°C.
- (3) Value is at 15°C.
- (4) Value is at 38°C.
- (5) Rough estimate from TPH fraction composition

Units:

atm-m<sup>3</sup>/mol: Henry's Law Constant mg/L

cp: centiPoise

g/cm<sup>3</sup>: gram per cubic centimeter

mg/L: milligram per liter

mm Hg: millimeter of mercury

*Solubility* is the measure of the ability of a hydrocarbon constituent to dissolve in water. The solubility of an individual petroleum constituent is generally dependent on the hydrocarbon class and the number of carbon atoms present in the compound (solubility within a given class of hydrocarbons decreases as the number of carbon atoms increases), combined with the proportion of the constituent in the whole mixture (see discussion of [effective solubility](#), in this chapter).

The tendency of a petroleum constituent to transfer from the liquid-mixture (NAPL) phase to the vapor phase is indicated by the vapor pressure of the individual compound. Chemicals having higher vapor pressure have a greater tendency to volatilize. As with solubility, the volatilization potential of an individual constituent will be dependent on the relative

proportion of that constituent in a petroleum mixture. Lower molecular-weight constituents have greater vapor pressure and volatility than higher molecular-weight constituents. The tendency of a constituent to move from the dissolved phase into the vapor phase is predicted by the Henry's Law Constant (H) for that constituent.

# Fate and Transport of Petroleum in the Subsurface

## Migration of LNAPL



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### Migration of LNAPL

When petroleum is released into the environment, it is typically released as a light non-aqueous phase liquid (LNAPL). LNAPLs (including most refined products and most crude oils) are liquids that are less dense than water. Not only are they less dense than water, but the LNAPL is an immiscible fluid, which means it must displace the air and/or water already residing in the soil pore spaces to move. This displacement and movement of LNAPL occurs when the pressure and/or the LNAPL saturation in the pore spaces is sufficiently high. The concentration of the LNAPL in the soil at the point when it becomes mobile is called the residual saturation.

These concepts are known as *relative permeability* and *relative saturation*; that is, LNAPL is not mobile until it occupies a threshold portion of the pore space. The technical components of relative permeability and relative saturation are discussed in detail in several references at the end of this chapter, including EPA 1995a. These properties vary, based on the product type and soil pore size. This section describes in general terms the migration of LNAPL in the vadose zone, the capillary fringe/smear zone, and man-made pathways.

#### In the Vadose Zone

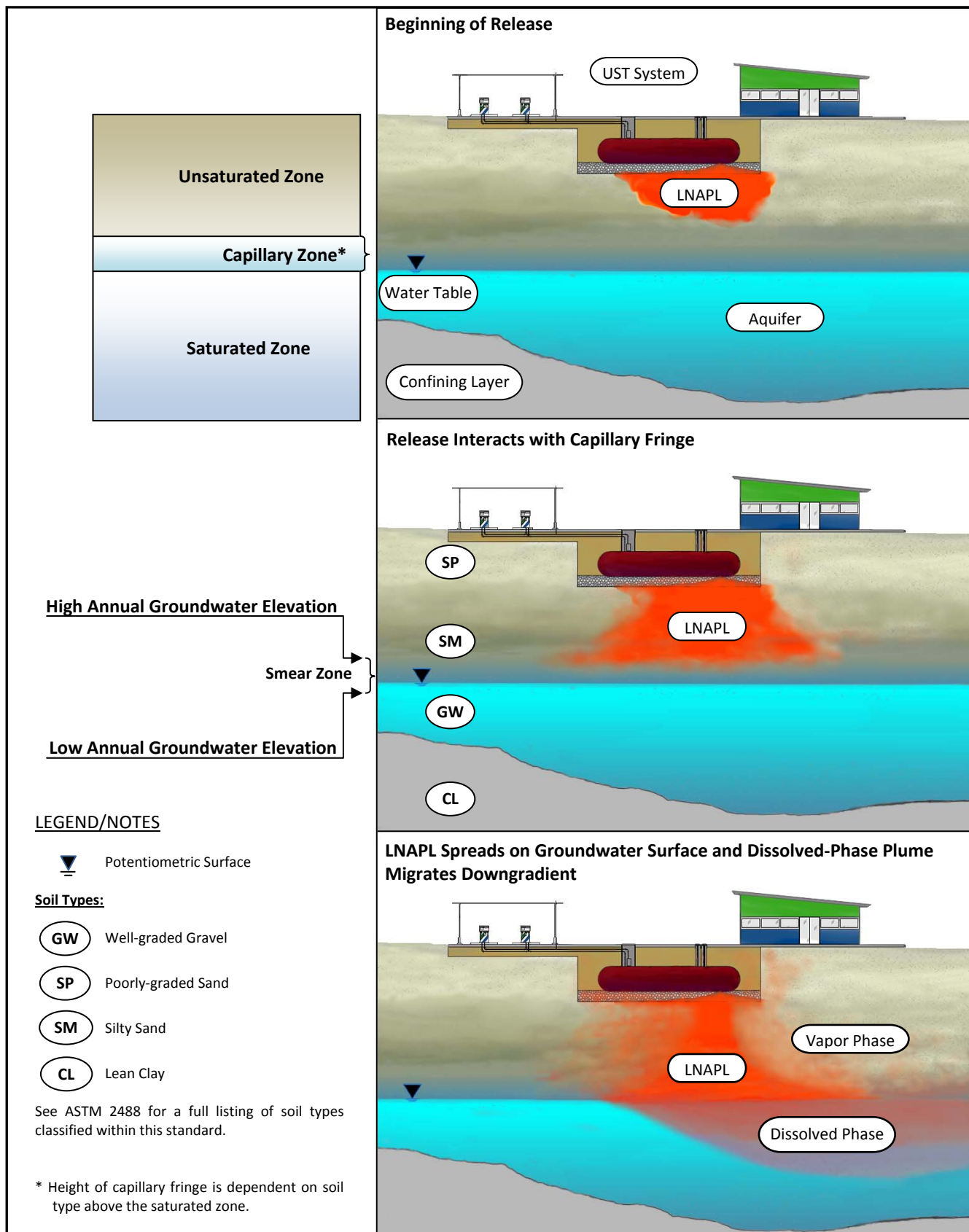
Following a petroleum release, LNAPL moves vertically downward through the unsaturated zone in response to gravity and capillary forces until it encounters either a relatively impermeable zone or the water table. The rate of migration is determined primarily by the stratification and permeability of the native soil materials. Some horizontal spreading will occur within the vadose zone as vertical migration proceeds because of capillary forces between the LNAPL and solid granular surfaces, as well as the varying hydraulic conductivities of subsurface materials.

Several factors, including the volume of the release, rate of the release, hydraulic conductivity of the soils, depth to the water table, and adsorptive capacity of the subsurface materials, will determine whether LNAPL will ultimately migrate downward to the area of the capillary fringe and the water table or remain entirely in the vadose zone. As LNAPL passes through the unsaturated zone, some LNAPL will remain behind in a residual (immobile) state, having been trapped by capillary forces (EPA 1995a; API 1996; Day 2001).

If a sufficient volume of LNAPL is released, it will migrate through the vadose zone to the water table and the capillary fringe (see Figure 1). As the LNAPL approaches the water table, it enters pore spaces that are of increasingly higher water saturation. Vertical or lateral movement of LNAPL through pore spaces of increasing water saturation at the capillary fringe depends on displacement of water from these pore spaces. This interface results in lateral migration of the LNAPL. The extent of lateral migration of LNAPL is controlled by the LNAPL head distribution and the relative saturation of LNAPL in the pore space.

In general, migration may be expected to be greatest in the direction of groundwater flow. Increasing LNAPL head or pressure is generally required to displace water within these zones, and LNAPL can migrate some distance below the water table if the pressure and saturation are great enough. Sharp interfaces between pore spaces saturated with LNAPL, water, and air generally do not exist within the subsurface at most sites (EPA 1995a). LNAPL will stop migrating when the pressure head is reduced and when the relative saturation of LNAPL becomes low enough.

Figure 1 - Progression of a Typical Petroleum Product Release from an Underground Storage Tank

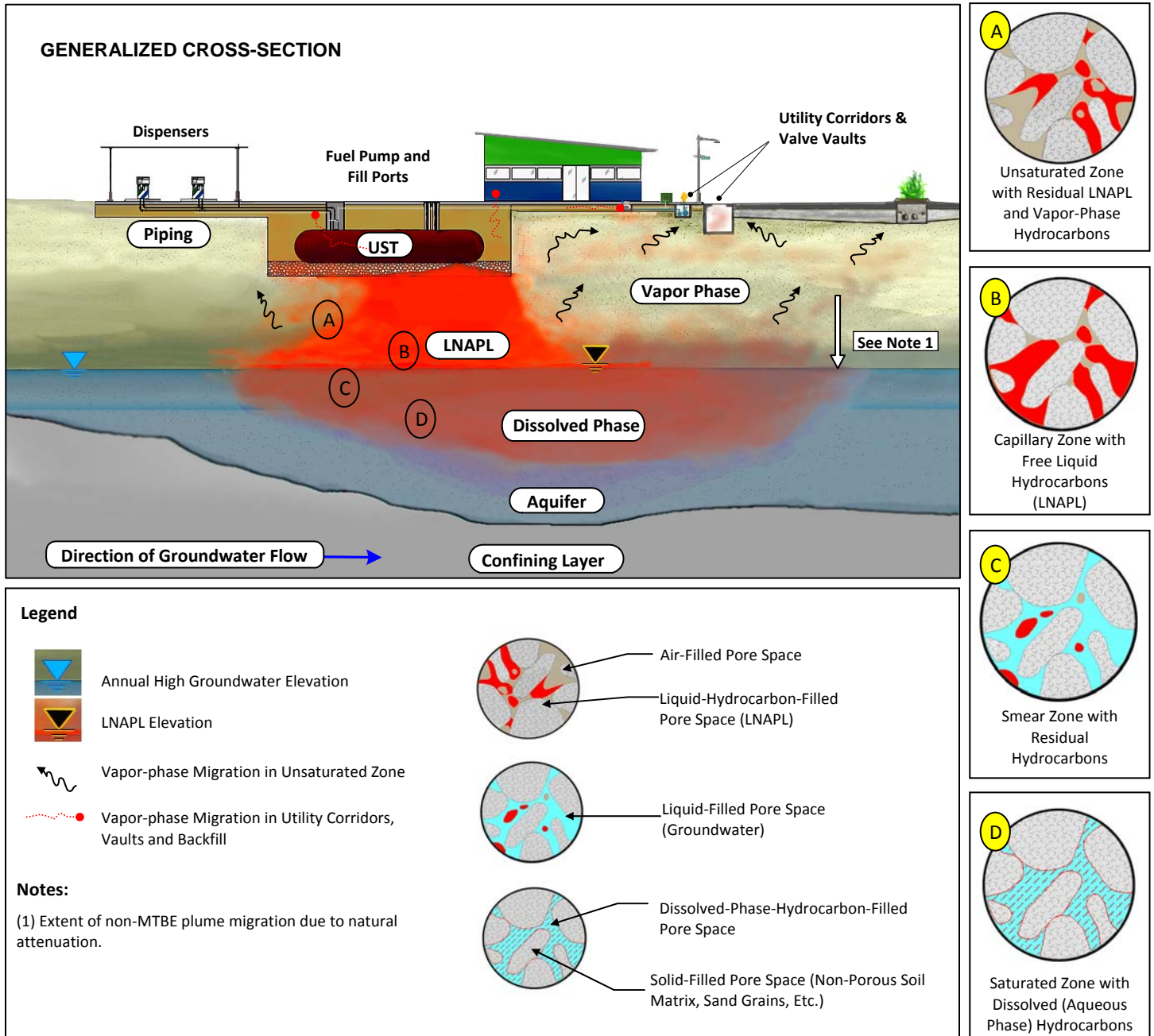




## In the Capillary Fringe/Smear Zone

Once the LNAPL equilibrates at the capillary fringe/ water table, it will be mobile if the relative saturation of LNAPL is high enough. Accumulations of LNAPL at or near the water table are susceptible to smearing within a vertical interval from fluctuations in water-table elevation due to seasonal changes or tidal influence. See Figure 2. LNAPL collected at the capillary zone will move downward as the water table drops because the soil pores drain off water, which allows the LNAPL to migrate. This leaves residual LNAPL in the expanded unsaturated zone above the new water table and an accumulation of LNAPL at the new capillary fringe. A subsequent rise of the water table will cause the capillary fringe and mobile LNAPL (if any) to move upward. Residual LNAPL can remain in the saturated zone below the raised water table because it is trapped behind water-filled pore spaces. This process results in LNAPL being distributed vertically between limits of high and low water levels and is called the *smear zone* (EPA 1995a; API 1996).

**Figure 2 - Vertical and Horizontal Distribution of Hydrocarbon Phases**





### Concept of Residual Saturation and Limits of LNAPL Mobility

As discussed above, LNAPL mobility is a function of its relative saturation, relative permeability, soil pore type and LNAPL viscosity. An important practical issue for LUFT sites is the question of, “At what concentration would the LNAPL potentially be mobile in the soil (flow due to gravitational force)?” This is known as *residual saturation*, and it is the concentration above which LNAPL may be mobile and below which LNAPL will not be mobile because it is trapped by capillary forces. Finer-grained soils result in a higher residual saturation concentration for a given LNAPL type, and more viscous LNAPLs result in higher residual saturation concentrations for a given soil type. There have been many studies evaluating the residual saturation concentrations for various LNAPLs in various soil types, and a good summary on the subject is the paper by Brost and DeVaul (2000). This paper recommends screening levels for residual saturation concentrations for various product types. The default soil type for the screening levels was medium to coarse sand. Brost and DeVaul’s screening-level (i.e., measured in coarse-grained material) residual saturation concentration for gasoline was 3,000 milligrams per kilogram (mg/kg); for diesel (“middle distillates”) it was 8,000 mg/kg; and for fuel oils it was 17,000 mg/kg.

However, the detailed data in Brost and DeVaul (2000) show that, as the soil type ranged from coarse gravel to silt, the residual saturation concentrations ranged from 1,000 to 10,000 mg/kg (for gasoline), from 2,300 to 23,000 mg/kg (for diesel), and from 5,100 to 51,000 mg/kg (for fuel oil). Therefore, it is very important to consider soil type when estimating a residual saturation concentration and potential LNAPL mobility at a LUFT site. Site-specific residual saturation concentrations can also be determined by testing of soil cores.

### LNAPL Migration through Man-Made Pathways

LNAPL can also move through man-made preferential pathways, such as improperly grouted monitoring wells, trenches containing distribution piping or utilities, or the backfill of trenches.

# Fate and Transport of Petroleum in the Subsurface

## Dissolution of Petroleum Hydrocarbons into Water



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Crude oils and refined products are extremely complex mixtures containing from hundreds to thousands of constituents. The portion of a fresh petroleum mixture (e.g., LNAPL) which is soluble and therefore dissolves into water consists of significantly fewer constituents, because the dissolved phase is a function of *effective* (as opposed to pure-phase) *solubility* of each individual constituent. This effective-solubility phenomenon is critical to understanding the groundwater plume from a petroleum release. This section of this chapter, drawn largely from Zemo and Foote (2003), discusses the constituents found within the dissolved phase of various products and the expected concentrations of each of those constituents.

### Pure-Compound Solubilities

Within a given molecular class, lower-molecular-weight petroleum constituents usually have higher pure-compound solubilities (Gustafson, et al. 1997; Mackay and Shiu 1992; Yaws, et al. 1990). Aliphatics have low pure-compound water solubilities at molecular weights exceeding six carbon atoms (C6). Monoaromatics (BTEX and alkylated benzenes) have higher pure-compound water solubilities, with the lowest molecular-weight compound (C6: benzene) having the highest relative pure-compound solubility. The lower molecular-weight PAHs (e.g., naphthalene [C10]) have low to very low pure-compound water solubilities, with the higher-molecular-weight PAHs (e.g., benzo(a)pyrene [C20]) being virtually insoluble in water.

For comparison, the following table shows the solubilities of various arrangements of C6 and C10 compounds. Note how the solubility of aliphatics is much lower than that of aromatics, even those with the same number of carbon atoms.

**Table 2 – Solubility of Various C6 and C10 Compounds**

Aromatic		Aliphatic	
Name	Solubility (mg/L)	Name	Solubility (mg/L)
C6 (Benzene)	1780	C6 (n-Hexane)	9.5
C10 (Naphthalene)	31	C10 (n-Decane)	0.052

### Effective Solubility

The composition and concentration of the dissolved phase from a mixture are controlled by the effective solubility of each constituent in the mixture. The effective solubility of each constituent is a function of its:

- Pure-compound solubility in water
- Mole-fraction within the mixture

Effective solubility dictates that the equilibrium concentration of each constituent within the dissolved phase of a petroleum product is significantly less than its pure-compound solubility, which means that, as a mixture, the individual components of the petroleum products are less able to dissolve into groundwater than those components would be if they were the only compound present.

## Drilling Down.

The effective solubility of petroleum constituents has been shown to follow Raoult's Law for ideal mixtures,

$$C_i = X_i * S_i$$

Where

$C_i$  = solute concentrations of component  $i$  (mg/L)

$X_i$  = mole fraction of component  $i$

$S_i$  = aqueous solubility of component  $i$  (mg/L)

and has been documented for petroleum in the literature (e.g., Cline, et al. 1991; Lee, et al. 1992; Shiu, et al. 1990; Mackay and Shiu 1992; Chen, et al. 1994; O'Reilly, et al. 2001; Huntley and Beckett 2002). The validity of these theoretical estimates and of the effective-solubility approach is supported by the laboratory research described below.

## Composition of Water Soluble Fractions (WSFs) from Laboratory Studies

The composition of the dissolved phase from fresh petroleum products (including gasolines, kerosenes, jet fuels, diesels, Bunker C fuel, and motor oils) and fresh crude oils has been investigated under laboratory conditions by several researchers using various analytical methods (e.g., Coleman, et al. 1984; Shiu, et al. 1990; Thomas and Delfino 1991; Bruya and Friedman 1992; Chen, et al. 1994; and Potter 1996).

The results from all of these studies are consistent, and provide clear evidence that the petroleum hydrocarbons, which comprise the measurable dissolved phase of fresh crude oil and fresh refined products, are limited primarily to these discrete constituents:

- C6 to C11 monoaromatics (BTEX and the alkylated benzenes)
- C10 to C14 PAHs (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene)
- C6 and smaller aliphatics

These studies focused on the hydrocarbon constituents of fresh crude oil and fresh refined products in the dissolved phase; however, the same principles apply to weathered products.

Blending agents or additives which are polar in their molecular structure, such as oxygenates, have both relatively high pure-compound solubilities *and* large mole-fractions within the product mixture; therefore, they can represent a large proportion of the dissolved phase of a given product. **This is why MTBE is present in plumes in much higher concentrations than the hydrocarbons.** Note that polar molecules have slightly charged negative and positive ends, and therefore are more soluble in water, which is also polar.

NSOs may be present in fresh crude oils or fresh fuel-oil products; thus, these polar compounds could comprise part of the dissolved phase of a fresh crude or fresh refined product, depending on the pure-compound solubility and its mole-fraction within the mixture.

## Important!

Thus, the components of fuel likely to be found in the dissolved phase include:

- C6 to C11 monoaromatics (BTEX and the alkylated benzenes),
- C10 to C14 PAHs (naphthalene, alkylated naphthalenes, acenaphthene, fluorene, phenanthrene, and anthracene),
- C6 and smaller aliphatics
- Polar blending agents/additives (such as MTBE)

## Concentration of WSFs from Laboratory Studies

In addition to evaluating the constituents within the dissolved phase, the Shiu, et al. (1990) and Potter (1996) studies investigated the maximum aggregate concentration of the dissolved phase (or bulk effective solubility) of fresh crude oils and fresh products. Excluding additives such as MTBE, the maximum aggregate concentration of the dissolved phase of fresh products tested is shown in the following table.

**Table 3 – Maximum Aggregate Concentration of Dissolved Phase of Fresh Products**

Product	Maximum Aggregate Concentration of WSF (mg/L)	Source
Gasolines	100 +	Shiu, et al. 1990; Potter 1996
Diesels and Fuel Oils	3 – 40	Shiu, et al. 1990; Potter 1996
Jet Fuels	15 – 65	Potter 1996
Bunker C	6	Shiu, et al. 1990
Fresh Crude Oils	10 – 58	Shiu, et al. 1990

With regard to concentrations of individual constituents in the dissolved phase, Zemo (2006) compiled data from up to nine laboratory partitioning studies which showed the average measured effective solubilities of BTEX from fresh gasoline, and from four laboratory studies which showed the average measured effective solubilities of BTEX from fresh diesel, as follows:

**Table 4 – Average Measured Effective Solubility from Fresh Gasoline and Fresh Diesel**

Average measured effective solubility (mg/L)		
	From fresh gasoline	From fresh diesel
Benzene	29	0.23
Toluene	36	0.58
Ethylbenzene	2.7	0.12
Xylenes	15	0.46

The data clearly show that the effective solubility of BTEX from fresh diesel sources is lower than that from fresh gasoline sources, because the mole-fraction of BTEX is much lower in diesel than in gasoline (see Zemo 2006 for a detailed discussion).

**Important!** Concentrations of any constituent in groundwater which significantly exceed its effective solubility, given a specific source type (especially for ethylbenzene and xylenes), indicate that a non-dissolved component (e.g., LNAPL) is likely present in the groundwater sample. Note that, for a weathered gasoline or diesel source, the effective solubilities will be even lower than for the fresh source.

### Effects of LNAPL Weathering on the WSF

The following discussion explains why weathered petroleum products are less soluble in groundwater.

As a crude oil or petroleum product weathers in the subsurface, both the constituents and the concentration of the dissolved phase associated with the weathered petroleum will change. As the original soluble constituents are leached out of the LNAPL or are biodegraded, their mole-fraction decreases within the remaining mixture, which further decreases their effective solubility and thus their concentration in the dissolved phase.

**For Example.**

The theoretical maximum concentration of dissolved benzene in water in the presence of fresh gasoline is about 18 mg/L, assuming that the benzene mole-fraction is 1% of the gasoline ( $1,780 \text{ mg/L} \times 0.01 = 17.8 \text{ mg/L}$ ). But if the gasoline is significantly weathered and the benzene mole-fraction is reduced to 0.1%, the theoretical maximum concentration of benzene in the WSF of the weathered gasoline is about 1.8 mg/L.

Ultimately, the residual petroleum mixture LNAPL becomes depleted of soluble constituents to the point where such constituents will no longer partition to the dissolved phase in measurable amounts. This was illustrated by Shiu, et al. (1990), when dramatic reductions in the measured aggregate WSF concentration were evidenced after laboratory evaporative “weathering” of crude oils and products. Most aggregate dissolved-phase concentrations of the weathered crude oil or product were reduced to about 1 mg/L or less, regardless of the original dissolved-phase concentration associated with the fresh oil or product. Accordingly, aggregate concentrations of dissolved petroleum hydrocarbons in groundwater at sites affected by highly weathered petroleum would not be expected to exceed about 1 mg/L in most cases, and could be non-detectable if the petroleum were sufficiently weathered (Zemo and Foote 2003).

# Fate and Transport of Petroleum in the Subsurface

## Migration of Dissolved-Phase Constituents



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Once LNAPL has come into contact with water and has partitioned individual constituents into the dissolved phase in accordance with effective solubility, those constituents will migrate. The dissolved-phase petroleum constituents migrate with groundwater at a rate controlled by advection and hydrodynamic dispersion. *Advection* is the transport of dissolved constituents by groundwater movement and is, therefore, dependent on the hydraulic conductivity and hydraulic gradient. *Dispersion* is the spread of dissolved constituents predominantly in the direction of groundwater flow, but also laterally and vertically to the direction of groundwater flow. Dispersion will tend to lengthen the plume and dilute the overall concentrations of dissolved constituents within the plume.

### Important!

Dissolved constituents are also affected by physical and chemical processes such as adsorption of the chemicals to subsurface materials. Dissolved-phase constituents are also affected by biodegradation. Hydrocarbon constituents are relatively easily biodegraded; ethers (e.g., MTBE) are less easily biodegraded. See *Biodegradation* section below.

*Sorption* is defined as the interaction of a chemical with a solid. Many parameters affect sorption, including solubility, polarity, ionic charge, pH, redox potential, and the organic carbon/water partition coefficient (Piwoni and Keeley 1990; EPA 1995b). The tendency to adsorb is different for each dissolved constituent, and is represented in transport equations by the soil partitioning coefficient,  $K_d$ . Sorption also causes the chemical to move more slowly than the bulk flow of water (retarded velocity). In general, finer-grained soils with greater clay content (higher organic content) retard the migration of dissolved hydrocarbons more than coarser-grained materials do.

All of these factors contribute to the ultimate length and width of the plume, and its concentrations over time. The combination of these factors (degradation and dispersion) is known as *natural attenuation* (discussed in the [Remediation](#) chapter.)

## Plume Extent and Concentration Studies at LUFT Sites

Three significant petroleum hydrocarbon multi-site plume studies were conducted in the 1990s (Rice, et al. 1995; Mace, et al. 1997; Groundwater Services, Inc. 1997). These three studies did not include MTBE. A relatively recent study of benzene and MTBE plume lengths at 500 UST sites in the Los Angeles area was published in 2004 (Shih, et al. 2004). This study showed that *the mean benzene plume length was 198 feet and that 90% of the benzene plumes were less than 350 feet long*.

A California study (by the Lawrence Livermore National Laboratory; Rice, et al. 1995) included 271 sites and showed that plume lengths change slowly, while average plume concentrations decline more rapidly. Plumes stabilize at relatively short distances from the fuel-release site. Ninety percent of the sites studied had plume lengths less than 255 feet. The study found that *hydrogeologic parameters have little relationship to plume length* (Rice, et al. 1995), indicating that biodegradation processes determine plume length and dominate the attenuation of the concentrations.

A Texas study evaluated 217 sites and found that most benzene plumes (75%) are less than 250 feet long and have either stabilized or are decreasing in length and concentration. *The study found that benzene plume length cannot be predicted on the basis of either site hydrogeology or previous remediation activities* (Mace, et al. 1997).

The Florida Risk-Based Corrective Action (RBCA) Planning Study analyzed groundwater data from 117 sites in 33 counties. The median plume length of the sites was 90 feet, based on BTEX data. Fifty-one percent of the sites in the study were at that time or had previously been subject to groundwater remediation (Groundwater Services, Inc. 1997). Approximately 75% of the petroleum plumes from the studies were less than 200 feet in length and were in a stable or shrinking condition (API 1998).

The addition of ethanol to gasoline at about 10% by volume may increase the length of a benzene plume by as much as 40% to 70%, based on plume-length studies conducted in Kansas and Iowa (Ruiz-Aguilar, et al. 2003). These studies showed the mean and median plume length for benzene from the two plume types as follows:

**Table 5 – Benzene Plume Length**

	Benzene Plume Length (feet)	
	Mean	Median
<b>Regular gasoline</b>	193	156
<b>EtOH-blended gasoline</b>	263	263

The benzene plume length increases in EtOH-blended gasoline because the ethanol is preferentially biodegraded over the hydrocarbons, which depletes the oxygen available in the source area. Benzene biodegrades fastest under aerobic conditions; therefore, its slower degradation rate under anaerobic conditions allows the plume to extend slightly longer. The length of the toluene plumes was not as impacted by the ethanol, most likely because toluene biodegrades relatively quickly under anaerobic conditions (see [Biodegradation](#) section below).

Plumes of MTBE can be longer than hydrocarbon plumes due to MTBE's high *effective solubility* in water, its mobility, and its lower natural biodegradation potential. Dissolved-phase MTBE plumes have been documented to be thousands of feet long, especially when conditions in the aquifer are neither aerobic nor methanogenic (Wilson 2003); but other plume studies have shown that MTBE plumes were only a few hundred feet long (Reisinger, et al. 2000). Shih, et al. (2004) showed that the MTBE plumes at 500 LUFT sites in the Los Angeles area had a mean length of 317 feet and that 90% of the plumes were less than 545 feet long.

### **Determining Groundwater Transport and Plume Length**

There are various analytical models in the public domain that can be used to estimate chemical transport time and plume lengths. These tools may be useful to evaluate plume stability, natural attenuation, and remediation time frame.



# Fate and Transport of Petroleum in the Subsurface



## Movement from LNAPL or Dissolved Phase into Vapor and Vapor Migration

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### Volatilization or Partitioning of Petroleum Constituents from LNAPL or Dissolved Phase into Vapor

Volatilization of petroleum hydrocarbons in the subsurface occurs via the volatilization of constituents that are in the dissolved phase (in pore water), volatilization from free-product LNAPL directly, and volatilization from the sorbed phase.

The partitioning between the dissolved and vapor phases is governed by Henry's Law. The tendency of the individual constituent to "escape" from the water phase to the vapor phase is proportional to its concentration in water, where the "proportionality constant" is the individual chemical's dimensionless form of the Henry's Law coefficient. This relationship assumes local equilibrium between water and air and is useful for estimating the potential for transport from water to air, and from vapor to water. For LNAPL, volatilization can also be described by the chemical's vapor pressure and Raoult's Law. The vapor pressure is a measure of the "escaping" tendency of individual constituents from the LNAPL mixture to the vapor phase. As with effective solubility, the volatilization of individual constituents from LNAPL is a function of the mole-fraction of the constituents within the mixture.

While both of these media (pore water and LNAPL) contribute volatiles to the vapor phase, it is usually assumed that, in the source region, all of the phases are in equilibrium with each other. In other words, the dissolved-phase concentrations already account for the chemical's mole fraction in the LNAPL. Therefore, for most chemicals, using either Henry's Law from pore water or Raoult's Law from LNAPL will yield the same concentration in vapor. Because of this, most *models* predict vapor-phase concentrations by first calculating the dissolved-phase concentration (using effective solubility due to mole fraction) and then using the chemical's Henry's Law coefficient, multiplied by the dissolved-phase concentration, to predict the vapor-phase concentration that will be in equilibrium with the LNAPL phase.

#### For Example.

If benzene is dissolved in groundwater, its tendency to volatilize can be predicted from its Henry's Law Constant and the concentration of benzene in pore water (or groundwater).

Recent empirical data are showing that the vapor phase associated with LNAPL is dominated by the aliphatic hydrocarbons, and not by the aromatic hydrocarbons. This is consistent with the relatively high mole-fractions and vapor pressures for the aliphatics, and the fact that the aromatics are more rapidly biodegraded, especially in the unsaturated zone.

#### Further Reading.

The following publications written by Dr. Blayne Hartman in the LUSTLine Bulletin discuss physical properties of petroleum hydrocarbons:

*Oh Henry (a constant)*. June 1998. LUSTLine Bulletin #29, pages 17-18.

*The Great Escape (from the UST)*. September 1998. LUSTLine Bulletin #30, pages 18-20.

*Which Compound Requires More Attorneys: MTBE or Benzene?* March 1999. LUSTLine Bulletin #31, pages 15-17.

*Some Enlightenment on Density*. June 1999. LUSTLine Bulletin #32, pages 24-25.

### Migration of Vapor-Phase Constituents

Once the individual constituents are in the vapor phase, they can continue to migrate in the vadose zone. Transport will occur through diffusion caused by concentration gradients; closer to the ground, surface advection becomes more important due to changes in temperature or barometric pressure. These changes may be induced inadvertently in basements of buildings, or intentionally at vapor-recovery wells. The greatest movement will take place in the most permeable materials (Bruce 1993).



In arid and semi-arid environments, the vadose zone will have relatively low moisture content over most of the year, and there is limited opportunity for volatilized constituents to dissolve into the water phase. If the soil-moisture content in the vadose zone is high, however, then relatively soluble compounds such as ethanol and MTBE will tend not to stay in the vapor phase, but rather will stay in the soil moisture (Day 2001).

The extent of migration of vapor-phase constituents is controlled by multiple natural attenuation processes, including biodegradation. Research has shown that vapor-phase petroleum constituents are usually biodegraded to very low or non-detectable concentrations within a few feet of the ground surface due to aerobic biodegradation, except in the case of high-concentration sources very close to and directly beneath the basement or slab of a building (Abreu, et al. 2009; Davis, et al. 2009).

## Vapor Intrusion

Vapor intrusion into buildings is one of the exposure pathways that needs to be evaluated for LUFT sites. This exposure pathway is usually evaluated using soil vapor measurements and models. For petroleum hydrocarbons (BTEX in particular) there have been many studies lately which indicate that BTEX impacting buildings is much less common than previously thought. The main reason for this is that BTEX readily degrades in the vadose zone, and the models historically used to evaluate this pathway did not include degradation processes. Degradation is also called *bioattenuation*.

Several modeling studies of petroleum vapor intrusion have evaluated the combined impact of oxygen demand and degradation rate on petroleum vapor intrusion (Parker 2003; Abreu and Johnson 2006; DeVaul 2007; Abreu, et al. 2009). The results from Abreu, et al. (2009) indicated that, for the conditions modeled, petroleum vapor attenuation was not oxygen-limited for vapor-source concentrations less than 10,000,000 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) (10 milligrams per liter [mg/L]). In the cases where degradation was not oxygen limited, the distance required between the building foundation and the dissolved petroleum source to ensure attenuation of high petroleum volatile organic compounds (VOCs) depended on the first-order degradation rate. When using the geometric mean biodegradation rate for aromatic hydrocarbons (0.79/hour), a separation distance between the source and the building of 1 m (3.28 feet [ft]) was sufficient to achieve 100x bioattenuation (i.e., a 100x increase in attenuation relative to the “no biodegradation” case), while a separation distance of 3 m (10 ft) resulted in 10,000x bioattenuation. When using the lower degradation rate (0.079/hour), a separation distance of 3 m (10 ft) was required to achieve 100x bioattenuation.

Modeling conducted by DeVaul (2007) indicates a similar range of bioattenuation. In this paper, DeVaul reports that the distance over which the concentration is reduced by 50% was on the order of 2.3 to 29 cm for benzene. The bioattenuation expected to occur over a distance of 3 m is at least 1000x (API 2009). These results are discussed in the publicly available BioVapor model (API 2009) based on DeVaul (2007). This model can be downloaded from the API web page at <http://www.api.org/>.

The available scientific literature related to petroleum vapor fate, transport, and intrusion into buildings suggests that:

- A number of mechanisms facilitate the transport of oxygen below building foundations, resulting in aerobic conditions at many sites, and
- Aerobic vadose-zone petroleum hydrocarbon biodegradation occurs wherever sufficient oxygen is present, resulting in rapid attenuation of hydrocarbon vapors over very short distances.

As a result, aerobic biodegradation often serves as a barrier to petroleum vapor intrusion into buildings at the majority of sites with sufficient separation between the source and the building foundation.

# Fate and Transport of Petroleum in the Subsurface

## Biodegradation

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Petroleum hydrocarbons are naturally biodegraded (oxidized) under both aerobic and anaerobic conditions, as documented in the literature. The simplest, most water-soluble constituents are biodegraded first (e.g., BTEX and the small *n*-alkanes); the more complex molecular structures are biodegraded more slowly. Also note that, for LNAPL, biodegradation only occurs at the air/oil and oil/water interfaces of the LNAPL, not in the center of the free product LNAPL. Both the vadose zone and the shallow saturated zone can evolve from aerobic conditions to anaerobic conditions at LUFT sites due to continuing biological activity. In most subsurface environments, both aerobic and anaerobic biodegradation of petroleum hydrocarbons can occur, often simultaneously, in different parts of the plume.

### Review of Redox Reactions

Redox reactions are the energy basis for biodegradation. Redox reactions (the common name for oxidation-reduction reactions) are fundamentally a set of reactions explaining the transfer of electrons between compounds. *Oxidation* is the half-reaction that involves the loss of electrons, and *reduction* is the half-reaction involving the gain of electrons. These reactions are always paired: oxidation and reduction happen virtually simultaneously.

The important aspect of redox reactions with regard to biodegradation is that they release energy which can be used for microbial growth. The more energy released in a redox reaction, the faster the microorganisms utilizing that reaction can grow.

Redox reactions involving hydrocarbons can derive the most energy from using oxygen as the *oxidizing agent* (also known as the electron acceptor). Anaerobic processes (those using anything other than oxygen as the oxidizing agent) release less energy, although as long as the reaction produces some amount of energy, it is still possible for microorganisms to utilize that energy. It should be noted, however, that different organisms are capable of utilizing different oxidizing agents, such that those organisms which degrade hydrocarbons by using oxygen as the oxidizing agent are different species from those using nitrate.

### Aerobic Biodegradation

Aerobic biodegradation is the breakdown of petroleum constituents by microorganisms (bacteria) using oxygen as the electron acceptor. Aerobic bacteria are usually indigenous to areas of the subsurface containing oxygen: the unsaturated zone and, if there is oxygen dissolved in the groundwater, the saturated zone. A reduction in dissolved oxygen concentrations within an existing BTEX plume is a strong indication that indigenous bacteria are already established and actively biodegrading petroleum constituents via aerobic respiration. Reduction of oxygen molecules is one of the most energetically favorable of the redox reactions involved in petroleum degradation. In general, dissolved-oxygen concentrations will be lower than background levels in groundwater that contains hydrocarbons.

Subsurface environments can become devoid of oxygen, especially if high concentrations of hydrocarbons are present. When this is the case, the rate of aerobic biodegradation will typically be limited by oxygen supply rather than by microorganism concentration. In any event, biodegradation of petroleum constituents occurs in most subsurface environments without the addition of supplemental bacteria (Wiedemeier, et al. 1995).

Low-molecular-weight aromatic hydrocarbons such as BTEX are easily biodegraded at the concentrations found dissolved in groundwater. *N*-alkanes between C10 and C22 are the most readily biodegradable hydrocarbon constituents. The biodegradation (redox) reaction causes the formation of a primary or secondary alcohol, with oxidation continuing to aldehydes and fatty acids for primary reactions, and to ketones and esters for secondary reactions (these are short-lived intermediate metabolites). The ultimate by-products of aerobic respiration are carbon dioxide and water.

### Anaerobic Biodegradation

Dissolved oxygen can be rapidly depleted by increased levels of microbial respiration after petroleum hydrocarbons enter the groundwater system, resulting in anaerobic conditions within the dissolved plume. Anaerobic microorganisms are usually indigenous to areas of the subsurface that are devoid of oxygen, usually the saturated zone and low-permeability areas of the unsaturated zone. Certain requirements must be met for anaerobic (also referred to as "anoxic") bacteria to

degrade petroleum constituents. These include the absence of dissolved oxygen, the availability of carbon sources (e.g., BTEX), electron acceptors, essential nutrients, and the proper ranges of pH, temperature, salinity, and redox potential. When oxygen is absent, nitrate, sulfate, iron(III), and carbon dioxide can serve as terminal electron acceptors (reduction).

During anaerobic degradation, BTEX compounds are first oxidized to phenols or organic acids, then transformed to long-chain volatile fatty acids, which are finally metabolized to carbon dioxide, methane, and water. Depending upon the type of electron acceptor present (nitrate, iron(III), sulfate, or carbon dioxide), pH conditions, and redox potential, anaerobic biodegradation can occur via denitrification, iron(III) reduction, sulfate reduction, or methanogenesis. Environmental conditions and microbial competition will ultimately determine which processes dominate but, in a typical aquifer, denitrification typically occurs first, followed by iron(III) reduction, sulfate reduction, and, finally, methanogenesis (Wiedemeier, et al. 1995).

### **Methyl Tert Butyl Ether (MTBE)**

There is increasing evidence that MTBE and TBA also naturally degrade under a variety of conditions, although not as rapidly as the BTEX compounds. At many sites, MTBE and TBA degrade under aerobic conditions; however, biodegradation of MTBE and TBA has also been reported under methanogenic, denitrifying, sulfate-reducing, and iron-reducing conditions (IRTC 2005).

### **Polar Non-Hydrocarbons in Groundwater Resulting from Biodegradation of Petroleum**

The metabolic by-products of petroleum biodegradation (e.g., alcohols, organic acids, phenols, aldehydes, ketones) have oxygen in their molecular structures and are therefore “polar” molecules, which are very soluble in water compared to the hydrocarbons.

The use of EPA Method 8015 for extractable total petroleum hydrocarbons (TPH; TPHd/mo or DRO/ORO) without silica-gel cleanup (SGC) has illuminated the finding that polar non-hydrocarbon compounds are generally present in groundwater at petroleum release sites where biodegradation is active. The polar compounds (“polars”) are measured in extractable TPH because they are extracted and quantified together with the hydrocarbons unless the sample extract is subject to a SGC to separate polars from hydrocarbons (Zemo and Foote 2003). Note that EPA Method 418.1 included a SGC to isolate the petroleum hydrocarbons, but when California transitioned to EPA Method 8015 in the early 1990s, the SGC was omitted. This resulted in the “improved” GC-FID method reverting back to a “total organics” measurement rather than a “petroleum hydrocarbon” measurement.

At the time of this writing, some in the regulatory community have been questioning whether these polars are likely to be less, equally, or more toxic than the most toxic petroleum constituents within the diesel range (C11 to C22 aromatics) and whether they may therefore pose a threat to groundwater quality. Because of the technical complexity of analyzing for these polars, the toxicity and organoleptic (taste and odor) properties of these polar non-hydrocarbons have not been well studied. The following box provides a common-sense assessment of their likely relative threat to the waters of the State.

## Drilling Down.

The polar compounds (polars) in groundwater at petroleum release sites are typically the by-products of biodegradation. During biodegradation, petroleum hydrocarbons are sequentially oxidized by microbes, first to alcohols and then to organic acids (which are both polar compounds), and then ultimately to carbon dioxide and water; short-lived intermediate metabolic by-products include phenols, aldehydes, and ketones (e.g., Barcelona, et al. 1995; Dragun 1998). The biodegradation of petroleum has been extensively studied for many years, and intrinsic and enhanced biodegradation is a widely-accepted remedial method for petroleum releases.

The mixture of specific polars present in the groundwater at a site where intrinsic biodegradation of petroleum is occurring is expected to be transient (i.e., it changes over time and space) due to changing oxidation/reduction (redox) conditions within the groundwater. Where studied, the organic acids have been shown to range from about 30% to more than 50% of the total amount of dissolved organic carbon present in groundwater downgradient from the petroleum release (Eganhouse, et al. 1993; Cozzarelli, et al. 1994; Thorn and Aiken 1998). The polar compounds also have been shown to naturally attenuate to carbon dioxide and water once the groundwater is sufficiently oxygenated (Eganhouse, et al. 1993; Cozzarelli, et al. 1994; Cozzarelli, et al. 1995).

Available empirical evidence (as measured at hundreds of sites in California by EPA Method 8015 DRO without silica-gel cleanup) indicates that the polars in groundwater are naturally limited in extent, laterally occurring in the vicinity of the LNAPL in the smear zone and downgradient for a few hundred feet downgradient, typically due to the anaerobic shadow caused by the intrinsic biodegradation. Polars also appear to be naturally limited in vertical extent. In areas where groundwater is sufficiently oxygenated, polars are no longer detected. Available empirical evidence also indicates that polar compounds do not persist in oxygenated surface water.

With respect to toxicity, comparison of the average reference doses (RfDs) for available constituents in the five classes of polar compounds most likely to be present in groundwater due to petroleum biodegradation indicates that polar compounds are likely of significantly lower toxicity than the C11 to C22 aromatic hydrocarbons, with the possible exception of alkylated phenols (if present).

Alkylated phenols have higher toxicity than the C11 to C22 aromatic hydrocarbons, but these are short-lived intermediate metabolites and are not expected to be present in significant concentrations. The other four groups of polars have average RfDs that are factors of 5 to 100 times higher than the C11 to C22 aromatic hydrocarbons.

With respect to organoleptic properties, comparison of odor thresholds for weathered and unweathered dissolved phases of gasoline and fuel oil #2 indicates that the polar compounds likely have higher taste and odor thresholds than the petroleum hydrocarbons (Gibbons 1940). Gibbons found that, after less than 20 days of weathering in an uncovered beaker, the odor of the water samples (which would consist largely of polar compounds after the weathering period) *decreased* by up to a factor of 10.

With respect to ecotoxicity, the polar by-products can be toxic to aquatic species in laboratory tests; however, field data show that these polars naturally attenuate very quickly and therefore pose little actual risk to ecosystems (Wolfe, et al. 1996).

Given the transient nature of polar compounds resulting from the biodegradation of petroleum, and the facts that

- (1) Empirical data show that these polars naturally attenuate because they are not persistent in oxygenated groundwater or surface water, and
- (2) Other available evidence suggests that they likely are less toxic and less odorous than the C11 to C22 aromatic fraction of the petroleum hydrocarbons,

these polars are considered to pose a relatively low risk to groundwater quality.

At this time, there is no evidence that polar compounds resulting from biodegradation of petroleum are creating a significant threat or nuisance to the waters of the State. Therefore, it is recommended that the focus of the State's resources and cleanup goals at petroleum release sites in California be the petroleum hydrocarbon constituents, and not the polar by-products of biodegradation.

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## References



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- Abreu, L.D.V., and P.C. Johnson. 2006. Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into Buildings: Influence of Degradation Rate, Source Concentration, and Depth. *Environ. Sci. Technol.* Vol. 40, No. 7: 2304-15.
- Abreu, D.V, R. Ettinger, and T. McAlary. 2009. Simulated Soil Vapor Intrusion Attenuation Factors Including Biodegradation for Petroleum Hydrocarbons. *Ground Water Monitoring & Remediation*, Winter 2009: 105-117.
- American Petroleum Institute (API). 1996. A Guide to the Assessment and Remediation of Underground Petroleum Releases. API Publication 1628, 3rd Edition. July.
- API. 1998. Characteristics of Dissolved Petroleum Hydrocarbon Plumes, Results from four studies. API Soil/Groundwater Technical Task Force, Vers. 1.1. December.
- API. 2009. Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into Buildings, Evaluation of Low Strength Sources Associated with Dissolved Gasoline Plumes. API Publication 4775. April.
- Barcelona, M.J., J. Lu, and D.M. Tomczak. 1995. Organic acid derivatization techniques applied to petroleum hydrocarbon transformations in subsurface environments. *Ground Water Monitoring and Remediation*, Spring: 114-124.
- Brost, E.J. and G.E. DeVaul. 2000. Non-Aqueous Phase Liquid (NAPL) Mobility Limits in Soil. *Soil and Groundwater Research Bulletin* No. 9. American Petroleum Institute.
- Bruce, L.G. 1993. Refined Gasoline in the Subsurface. *The American Association of Petroleum Geologists Bulletin*. Vol. 77, No: 212-224.
- Bruya and Friedman. 1992. Don't make waves: Analysis of water samples for total petroleum hydrocarbons. *Soils*. January-February: 6-7 and 46-47.
- Chapelle, F.H. 1999. Bioremediation of petroleum hydrocarbon-contaminated ground water: The perspectives of history and hydrology. *Ground Water*, 37(1), 122-132.
- Chen, C.S.H., J.J. Delfino, and P.S.C. Rao. 1994. Partitioning of organic and inorganic components from motor oil into water. *Chemosphere* 28, No. 7: 1385-1400.
- Cline, P.V., Joseph Delfino, and P.S.C. Rao. 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. *Environ. Sci. Technol.* Vol. 25, No. 5, 914-920.
- Coleman, W.E., J.W. Munch, R.P. Streicher, P. Ringhand, and F. Kopfler. 1984. The identification and measurement of components in gasoline, kerosene and No. 2 fuel oil that partition into the aqueous phase after mixing. *Arch. Environ. Contam. Toxicol.* 13: 171-178.
- Cozzarelli, I.M., M.J. Baedecker, R.P. Eganhouse, and D.F. Goerlitz. 1994. The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in groundwater. *Geochimica et Cosmochimica Acta*, Vol. 58, No. 2: 863-877.
- Cozzarelli, I.M., J.S. Herman, and M.J. Baedecker. 1995. Fate of microbial metabolites of hydrocarbons in a coastal plain aquifer: the role of electron acceptors. *Environmental Science and Technology*, Vol. 29, No. 2: 458-469.
- Davis, G.B., B.M. Patterson, and M.G. Trefry. 2009. Evidence for instantaneous oxygen-limited biodegradation of petroleum hydrocarbon vapors in the subsurface. *Ground Water Monitoring & Remediation*, Vol. 29, No. 1: 126-137.
- Day, M.J. 2001. The fate and transport of oxygenates and other petroleum constituents, and their influence on appropriate underground storage tank management. *Contaminated Soil Sediment and Water*. August. pp. 14-19.
- Dragun, J. 1998. *The Soil Chemistry of Hazardous Materials*, 2nd ed. Amherst Scientific Publishers.
- DeVaul, G.E. 2007. Indoor Vapor Intrusion with Oxygen-Limited Biodegradation for a Subsurface Gasoline Source. *Environ. Sci. Technol.* Vol. 41: 3241-48.

- Eganhouse, R.P. and M.J. Baedecker, I.M. Cozzarelli, G.R. Aiken, K.A. Thorn, and T.F. Dorsey. 1993. Crude oil in a shallow sand and gravel aquifer – II. Organic geochemistry. *Applied Geochemistry*. Vol. 8, Iss. 6: 551-567.
- U.S. Environmental Protection Agency (EPA). 1995a. Light non-aqueous phase liquids. Ground Water Issue. EPA/540/S-95/500. 28 pages.
- EPA. 1995b. How to evaluate alternative cleanup technologies for underground storage tank sites – a guide for corrective action plan reviewers. EPA 510-B-95-007. May.
- EPA. 1996. How To Effectively Recover Free Product At Leaking Underground Storage Tank Sites: A Guide For State Regulators (EPA 510-R-96-001). Available at: <http://www.epa.gov/OUST/pubs/fprg.htm>
- EPA. 1997. Expedited site assessment tools for underground storage tank sites - a guide for regulators. EPA 510-B-97-001. March. Available at: <http://www.epa.gov/oust/pubs/sam.htm>
- EPA. 1999. Monitored Natural Attenuation of Petroleum Hydrocarbons; Remedial Technology Fact Sheet. Available at: <http://www.clu-in.org/download/remed/pet-hyd.pdf>
- EPA. 2009. Modeling Subsurface Petroleum Hydrocarbon Transport. Retrieved Aug. 24, 2009, from <http://www.epa.gov/athens/learn2model/>
- Gibbons, M.M. 1940. Water pollution by petroleum oils. *Journal of the American Water Works Association* 32: 465-477.
- Groundwater Services, Inc. 1997. Florida RBCA Planning Study. [www.GSI-net.com](http://www.GSI-net.com)
- Gustafson, J.B., T.J. Griffith, and D. Orem. 1997. Selection of representative TPH fractions based on fate and transport considerations. Total Petroleum Hydrocarbon Criteria Working Group Series, Vol. 3. Amherst Scientific Publishers, Massachusetts.
- Happel, A.M., E.H. Beckenbach, R.U. Halden. 1998. An evaluation of MTBE impacts to California groundwater resources. Lawrence Livermore National Laboratory. UCRL-AR-130897. June.
- Huntley, D. and G.D. Beckett. 2002. Persistence of LNAPL sources: relationship between risk reduction and LNAPL recovery. *Journal of Contaminant Hydrology*. Vol. 59, Nos. 1-2, 3-26.
- Interstate Technology & Regulatory Council (IRTC). 2005. Overview of groundwater remediation technologies for MTBE and TBA. Technology Overview. February. <http://www.irtcweb.org/Documents/MTBE-1.pdf>
- Lee, L.S., M. Hagwall, J.J. Delfino, and P.S.C. Rao. 1992. Partitioning of polycyclic aromatic hydrocarbons from diesel fuel into water. *Environmental Science and Technology*. Vol. 26, No. 11: 2104-2110.
- Mace, R.E., R.S. Fisher, D.M. Welch, and S.P. Parra. 1997. Extent, mass, and duration of hydrocarbon plumes from leaking petroleum storage tank sites in Texas. Bureau of Economic Geology, Geological Circular 97-1.
- Mackay, D., and W.Y. Shiu. 1992. Estimating the multimedia partitioning of hydrocarbons: The effective solubility approach. In *Hydrocarbon Contaminated Soils and Groundwater 2*, E.J. Calabrese and P.T. Kosteki, editors. 137-154. Lewis Publishers.
- Moyer, E.E. 2003. Chemical and Physical Properties. Chapter 2 of MTBE Remediation Handbook, E.E. Moyer and P.T. Kosteki, editors. Amherst Scientific Publishers, Amherst, MA.
- Mulroy, Patrick T. and Li-Tse Ou. 1998. Degradation of tetraethyllead during the degradation of leaded gasoline hydrocarbons in soil. *Environmental Toxicology and Chemistry*, Vol. 17, No. 5: 777-782.
- O'Reilly, K.T., R.I. Magaw, and W.G. Rixey. 2001. Predicting the effect of hydrocarbon and hydrocarbon-impacted soil on groundwater. American Petroleum Institute No. 14. September.
- Parker, J.C. 2003. Modeling volatile chemical transport, bio-decay, and emission to indoor air. *Ground Water Monitoring & Remediation*, Vol. 23, No. 1: 107-120.
- Pasteris, G., D. Werner, K. Kaufmann, and P. Höhener. 2002. Vapor phase transport and biodegradation of volatile fuel compounds in the unsaturated zone: a large scale lysimeter experiment. *Environ. Sci. Technol.* Vol. 36, No. 1, 30-39.
- Piwoni, M.D., and J.W. Keeley. 1990. Basic concepts of contaminant sorption at hazardous waste sites, Ground Water Issue, EPA/540/4-90/053, 7 pp.



- Potter, T.L. 1996. Analysis of petroleum-contaminated water by GC/FID with direct aqueous injection. *Ground Water Monitoring and Remediation*. Summer. 157-162.
- Reisinger, H.J., J.B. Reid, and P.J. Bartholomae. 2000. MTBE and benzene plume behavior - A comparative perspective. *Soil Sediment & Groundwater MTBE Special Issue*. pp. 43-46.
- Rice, D.W., R.D. Grose, J.C. Michaelsen, B.P. Dooher, D.H. MacQueen, S.J. Cullen, W.E. Kastenber, L.G. Everett, M.A. Marino. 1995. California leaking underground fuel tank (LUFT) historical case analyses. Lawrence Livermore National Laboratory. UCRL-AR-122207. November.
- Ruiz-Aguilar, G.M.L., K. O'Reilly, and P.J.J. Alvarez. 2003. A comparison of benzene and toluene plume lengths for sites contaminated with regular vs. ethanol-amended gasoline. *Ground Water Monitoring & Remediation*. Vol. 23, No. 1: 48-53.
- Santa Clara Valley Water District (SCVWD). 2000. An evaluation of MtBE occurrence at fuel leak sites with operating gasoline USTs. Santa Clara Valley Water District. May.
- Shih, T., Y. Rong, T. Harmon, and M. Suffet. 2004. Evaluation of the impact of fuel hydrocarbons and oxygenates on groundwater resources. *Environmental Science & Technology*. Vol. 38, No. 1: 42-48.
- Shiu, W.Y., M. Bobra, A.M. Bobra, A. Maijanen, L. Suntio, and D. Mackay. 1990. The water solubility of crude oils and petroleum products. *Oil and Chem. Poll.* Vol. 7, No. 1, 57-84.
- State of California, State Water Resources Control Board (SWRCB). 1995. Letter LG 141: Permanent hydraulic fuel tank exemption. To: Local Agencies. November 14.
- SWRCB. 1995. Report on hydraulic lift tanks: A report to the California legislature on the effect upon the environment of hydraulic lift tanks. February.
- Thomas, D.H., and J.J. Delfino. 1991. A gas chromatographic/chemical indicator approach to assessing ground water contamination by petroleum products. *GWMR*. Fall. 90 et seq.
- Thorn, K.A. and G.R. Aiken. 1998. Biodegradation of crude oil into nonvolatile organic acids in a contaminated aquifer near Bemidji, Minnesota. *Organic Geochemistry*, Vol. 29, Issue 4: 909-931.
- United States Environmental Protection Agency (USEPA). 2010. Regional Screening Levels (Formerly PRGs). <http://www.epa.gov/region9/superfund/prg/>
- Wiedemeier, T., J.T. Wilson, D.H. Kampbell, R.N. Miller, and J.E. Hansen. 1995. Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination dissolved in groundwater. Volume 1. Air Force Center for Environmental Excellence, Technology Transfer Division. November. <http://www.afcee.af.mil/shared/media/document/AFD-071211-039.pdf>
- Wolfe, D.A., K.J. Scott, J.R. Clayton, Jr., J. Lunz, J.R. Payne, and T.A. Thompson, 1996. Comparative toxicities of polar and non-polar organic fractions from sediments affected by the Exxon Valdez oil spill in Prince William Sound, Alaska. *Fate and Toxicity of Spilled Oil from the Exxon Valdez, Exxon Valdez Oil Spill State/Federal Natural Resource Damage Assessment Final Report (Subtidal Study Number 4)*, NOAA, Office of Ocean Resources Conservation and Assessment, Silver Spring, MD: 52-78.
- Yaws, C.L., H.-C. Yang, J.R. Hopper, and K.C. Hansen. 1990. 232 hydrocarbons: Water solubility data. *Chemical Engineering*. 177-182.
- Zemo, D.A. and G.R. Foote. 2003. The technical case for eliminating the use of the TPH analysis in assessing and regulating dissolved petroleum hydrocarbons in ground water. *Ground Water Monitoring & Remediation*, Vol. 23, No. 3: 95-104.
- Zemo, D.A. 2006. Sampling in the smear zone: Evaluation of non-dissolved bias and associated BTEX, MTBE and TPH concentrations in ground water samples. *Ground Water Monitoring & Remediation*, Vol. 26, No. 3: 125-133.

### Further Reading.

Modeling Subsurface Petroleum Hydrocarbon Transport: <http://www.epa.gov/athens/learn2model/>

# Conceptual Site Model

Version 1.0 – Draft August 2010



## Scope of This Chapter

This chapter discusses the Conceptual Site Model (CSM) and the integral part it plays in evaluating risk and guiding decisions regarding the investigation and remediation of LUFT sites.

Evaluating risk at a LUFT site involves making a estimate of the current or likely future risk to human health, safety, and the environment associated with contamination at the site. Evaluating risk should be a preliminary activity at a LUFT site because it helps in making decisions as to whether investigation and corrective action are necessary (risk management).

Risk evaluation starts with the development of a good CSM which identifies the source(s) of contamination, the potential receptors, and the migration pathways.

This first part of this chapter describes the various components of a CSM including the source(s), pathways, and receptors. Then, the four typical exposure scenarios that could potentially exist at LUFT sites are described, including a few examples showing the development and refinement of the CSM.

## Conceptual Site Model

Most people think of a CSM as a tangible document, graphic, or depiction. It is the intent of the LUFT Manual to change that perception and help stakeholders understand that a CSM is a thought process that is always implemented at a LUFT site, whether or not it is recorded on paper. The goal of this chapter is to help responsible parties (RPs), consultants, and regulators consider all of the pieces of a CSM, regardless of whether the model exists in the mind of the stakeholder, in a diagram, or in a written description.

When developing his Theory of Relativity, Albert Einstein developed a conceptual model by visualizing events and interactions that were too big (or too small) to be performed as conventional experiments in a laboratory. The process of starting to evaluate LUFT sites is similar, in that the subsurface release exists underground and only small pieces of information are available to the environmental professional. The actual spill and distribution of the source are hidden from view underground and are too complex to model in the laboratory. To discuss and make decisions about LUFT sites, one must visualize the source and the movement of contaminants in the subsurface and create a model or analogy. This is the “conceptual model.” Although the term “conceptual site model” is not found in California law or regulations, the thought process is fundamental to scientific inquiry and is directly applicable to decision-making at LUFT sites.

The objectives of a CSM are:

- To convey an understanding of the origin, nature, and lateral and vertical extent of contamination.
- To identify potential contaminant fate-and-transport processes and pathways. See the [Fate and Transport](#) chapter for further details.
- To identify potential human and environmental receptors that may be impacted by contamination associated with the site.
- To guide site investigation activities and identify additional data needed (if any) to draw reasonable conclusions regarding the source(s), pathways, and receptors.
- To evaluate risk to human health, safety, and the environment posed by releases at a LUFT site.

These objectives emphasize the need for an approach where a CSM is developed early and is iteratively refined through the project life cycle. Each piece of data that is collected should serve to refine the CSM. The Interstate Technology & Regulatory Council (ITRC) Vapor Intrusion Pathway Guideline document (ITRC 2007) provides additional information on developing a CSM.

## Initial CSM

An initial CSM should be developed prior to any investigative work at a LUFT site. The initial CSM provides a general idea of conditions at the site and indicates what type of additional information, if any, may be needed to determine the degree of risk associated with the site.



To develop an initial CSM, readily available information about the site, the nature and quantity of the release, and preliminary information regarding the migration pathways and potential receptors are gathered. Data may also be collected from available sources concerning surrounding populations, such as ambient water quality, use and approximate locations of nearby wells, sub-surface soil conditions, locations of subsurface utilities, climatological conditions, and land use. LUFT sites on nearby properties can be a good source of information; if there are nearby LUFT sites, this information can often be readily obtained from the GeoTracker system via the Internet (see the [GeoTracker](#) chapter).

### **CSM and Site Assessment**

The initial CSM should be used to guide the site-assessment activities. Any part of the CSM with significant uncertainty should be investigated to gain a better understanding and to refine the CSM. For example, the potential migration pathways may need to be investigated to determine whether or not they may be complete.

### **CSM and Risk Management**

Once environmental samples are collected and analytical data are available during site assessment (or other phases of work, such as verification sampling during remediation, or confirmation sampling after a remedial action), the data are usually compared to established screening levels to determine whether further risk evaluation is necessary. This is discussed in further detail in the [Risk Evaluation and Risk Management](#) chapter.

### **CSM and Corrective Action**

If the information gained during the site assessment and risk evaluation indicates that the site may pose a current or future threat to human health, safety, and/or the environment, remediation or other corrective actions may be performed to mitigate the adverse effects of the release. The CSM is used to guide remediation decisions and to ensure that potential receptors' exposures are appropriately eliminated or mitigated. The [Remediation](#) chapter discusses several common remedial technologies employed at LUFT sites.

### **Updating the CSM**

As additional information becomes available during site investigation or the site conditions change because of remediation, implementation of engineering controls, or other physical changes, the CSM should be re-evaluated and updated to incorporate the new data and any new understanding of the site conditions. At any time during the process, if the regulatory agency determines that the site does not pose a threat to human health, safety, and/or the environment, the agency may suspend site characterization or cleanup activities at the site and send a letter stating that no further action is required.

## **Development of the CSM**

Development of a CSM begins with a general understanding of the environment in which the LUFT site is found and the sources of potential contaminants. From there, the CSM describes the potential ways in which the contaminants may migrate in the environment and the receptors that may ultimately be affected. The following discussion includes things to consider when developing the CSM.

### **Hydrogeologic Setting**

The geology at a site, and its stratigraphy, structure, and morphology, all affect the migration behavior of a subsurface release at that site. Gaining an understanding of the geologic setting will also help to determine the pathways of migration. Much of the geologic information for a LUFT site can be gathered from historical reports, state and federal environmental databases, and electronic and paper files covering the site and adjacent properties from various federal, state, and local agencies. Geologic aspects to consider when conceptualizing the geology at a LUFT site include:

- Site topography.
- Regional and local geologic conditions.
- Site-specific soil texture/lithology (e.g., identify the predominant types of soil at the site, such as clay, sand, gravel, fractured rock, sediments, etc.), stratigraphy, and structures (e.g., dipping strata) that may affect contaminant occurrence and extent.

An understanding of the regional hydrology is also important in developing the CSM, especially if groundwater could potentially become impacted or is already impacted. Hydrogeologic features to be considered when developing the CSM include:

- Depth to the water table and its seasonal and known historical fluctuation.
- Groundwater flow in the shallowest aquifer (gradient direction, hydraulic conductivity) including, perhaps, any vertical component and inter-connectedness of aquifers.
- Whether or not the source is beneath a low-permeability surface (such as asphalt or concrete).
- Designated beneficial uses of groundwater beneath the site.

## Source

For purposes of evaluating risk, the source is defined as the environmental medium/media containing elevated contaminant concentrations associated with the release. Some risk-based corrective action (RBCA) programs define the source to be the original cause of the contamination. Usually, by the time a site becomes a LUFT site, however, the original source has been eliminated and the current source of contamination is soil and/or groundwater. Items to consider when conceptualizing the source are included in the list below. Some of the specifics may be determined based on historical information; others will need to be determined during site assessment.

- The origin(s) of the release (e.g., a leaking UST, dispenser, product piping, and/or surface spill).
- The number of USTs, the capacity of the tanks (e.g., 12,000 gallons), the products stored, the date of installation, and the removal date(s) (if applicable).
- The location of historical and active USTs, dispensers, and product piping.
- Details about the specific release location(s) (e.g., spill locations, and time frame/dates if known).
- The type of fuel released and the constituents of concern (COCs) associated with the fuel. The [Fate and Transport](#) chapter of this Manual presents guidance on identifying potential COCs associated with fuel.
- The historical use of fuel additives (e.g., methyl tertiary butyl ether [MTBE] or other fuel oxygenates, lead, lead scavengers).
- The media that are impacted (e.g., soil, groundwater).
- Other potential sources such as surfaces spills, AST leakage, or pipeline leakage.

The information needed to define the source, obtained during the site assessment, include the following:

- Lateral and vertical extent of:
  - LNAPL
  - COCs in unsaturated-zone soil
  - COCs in saturated-zone soil and the smear zone
  - COCs in groundwater
- The concentration distributions of the COCs in the impacted media.

After evaluating the information obtained during site characterization, the extent and magnitude of the contamination can be defined. This is not an exact science; usually some assumptions will need to be made. In these cases, it is important, from a risk evaluation perspective, to be conservative.

## Exposure Pathways

Pathways are the mechanisms by which a receptor may contact the COCs at a site. Exposure pathways consist of three parts: (1) a source of contaminants (as described previously), (2) an exposure point where the receptor may come into contact with contaminants, and (3) an exposure route (such as ingestion or inhalation).

The [Fate and Transport](#) chapter of this Manual provides guidance on the various phases of petroleum constituents and how they behave in the subsurface. This information is critical for evaluating migration pathways or indirect exposure pathways. Typical migration pathways for LUFT sites include:

- LNAPL migration from the source area through soil.
- Dissolved-phase migration of COCs in the groundwater zone.
- Vapor migration of COCs from soil, groundwater, or LNAPL.
- Migration of COCs with groundwater and discharging of COCs to surface water.

In the surface-water example, the receptors may include ecological receptors as well as human receptors.

## Points of Exposure

A “point of exposure” is where a receptor comes into contact with contamination. The exposure point may, or may not, be at the same location as the source. Examples of points of exposure include:

- Surface soil
- Water faucet used for drinking water
- Air inside a residence

## Exposure Route

Exposure routes are the mechanisms by which receptors may come into contact with contamination. Exposure routes at LUFT sites include:

- Dermal contact with contaminated soil
- Ingestion of contaminated soil
- Ingestion of contaminated groundwater
- Inhalation of vapors (in indoor air) from contaminated soil, groundwater, or LNAPL

While developing the CSM, each of the elements of a pathway should be considered and investigated as necessary. For example, if groundwater at the site is not potable and the COCs in groundwater are not expected to migrate and impact a current or future potable water source above established limits, then the groundwater migration pathway may be eliminated.

## Receptors

A receptor is a human or other living organism with the potential to be exposed to and adversely affected by contaminants as a result of contact with contaminated media either at the source or along a contaminant migration pathway. Potential receptors at LUFT sites may include:

- Adults and children in a residential scenario
- Adults in an occupational scenario
- Adults in a construction/utility worker scenario
- Adults and children using groundwater that has been contaminated by a release at the site as a potable water supply

“Sensitive” human receptors are not evaluated separately because the USEPA toxicity values used in risk evaluations already consider sensitive subgroups.

Ecological receptors may also be potential receptors, but considering that LUFT sites are typically small, paved, and located in largely urban and/or otherwise disturbed environments, significant impacts to ecological receptors are unlikely to occur in most cases. Situations in which potential impacts to ecological receptors may warrant evaluation include cases in which impacted groundwater may migrate and discharge to nearby surface-water bodies and cases in which the LUFT site is located in areas where special status ecological receptors may reside.

## Receptor Identification

It is important to consider the current and reasonably likely future uses of the site and adjacent properties when identifying receptors. Local zoning and planning agencies can generally assist in these determinations. Determining conditional uses at the LUFT site and adjacent properties is important, because changes in use may require consideration of different receptors. For example, a light-industrial park being re-developed for residential living needs to be evaluated for both adults and children who may live on the property.

The types of potential receptors located on adjacent properties should be identified if they could come onto the site or be exposed to the chemicals at the site. The extent of the area where receptors should be identified will vary based on the exposure pathways as well as the extent and type of contamination.

At LUFT sites that are currently operating (e.g. as a gas station) and that are expected to remain in operation into the foreseeable future, on-site workers should be addressed separately from off-site workers. On-site workers at these facilities are protected by occupational exposure and hazard communication programs administered by appropriate regulatory authorities and potential exposures to those workers are outside the scope of the LUFT program. If the site is an operating

service station, for example, and air quality is being monitored for the worker, then the vapor-intrusion pathway may not need to be considered.

In order to identify whether receptors may be drinking potentially impacted groundwater, a survey of water-supply wells near the site may be conducted. (See the [Fate and Transport](#) chapter for more information on potential plume lengths.) This survey is generally based on reviewing Department of Water Resources (DWR) well records and asking local water district and applicable City and/or County staff if they are aware of any wells within the search radius. Areas with known multiple private wells nearby may require door-to-door contact of local residents to determine their source of water.

Information about water-supply wells can often be obtained from the well owner. Desired information includes:

- Current status of the well (operational or idle) and pumping rate.
- Purpose of the well, such as drinking water, irrigation, industrial, livestock, etc.
- Well construction details (i.e. the depth and length of the well screen).

**Groundwater as a Receptor?** In California, many Regional Board basin plans have designated almost all groundwater as a potential drinking-water source, and water quality objectives (WQOs) are applied as cleanup goals. When this standard is applied at all points in the aquifer, the effect is that groundwater has been considered a receptor; however, in this Manual, a “receptor” is defined as a living organism that is evaluated in a risk assessment.

### Example CSMs for LUFT Sites

Typical LUFT sites will have four basic exposure scenarios involving typical combinations of source media, exposure media, and receptors:

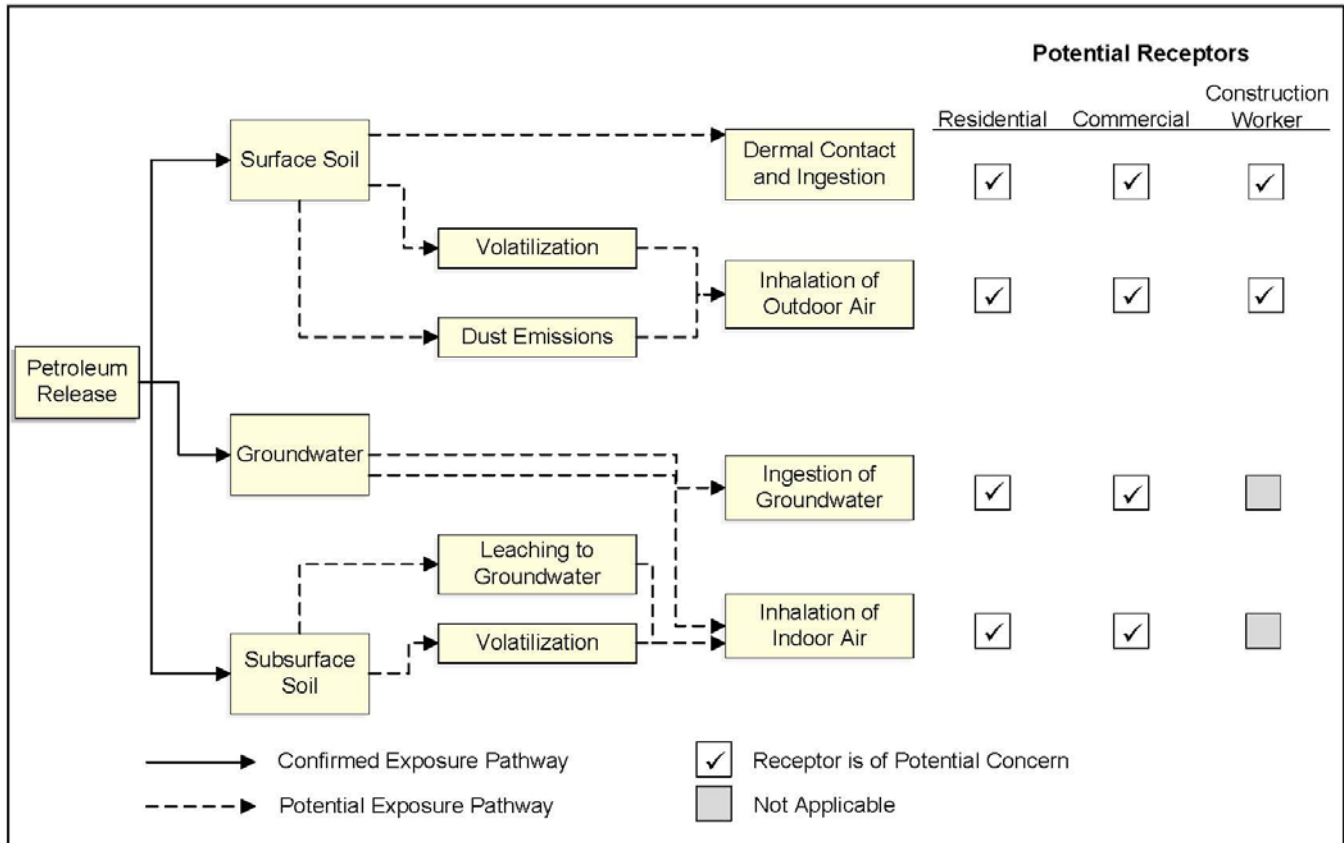
- Dermal contact with soil,
- Volatilization from impacted soil or groundwater into indoor air,
- Leaching from soil to groundwater,
- Groundwater that is already impacted above water quality objectives (WQOs).

These four exposure scenarios are discussed in more detail in the [Risk Evaluation and Risk Management](#) chapter.

#### Initial CSM

Figure 3 shows an initial CSM for a former gas station where a release has been identified; however, no site characterization has occurred. In this case, all four exposure scenarios may be possible at the site and are therefore presented in the diagram.

Figure 3 - Example of an Initial CSM When No Site Information Is Available



Conceptual Site Model

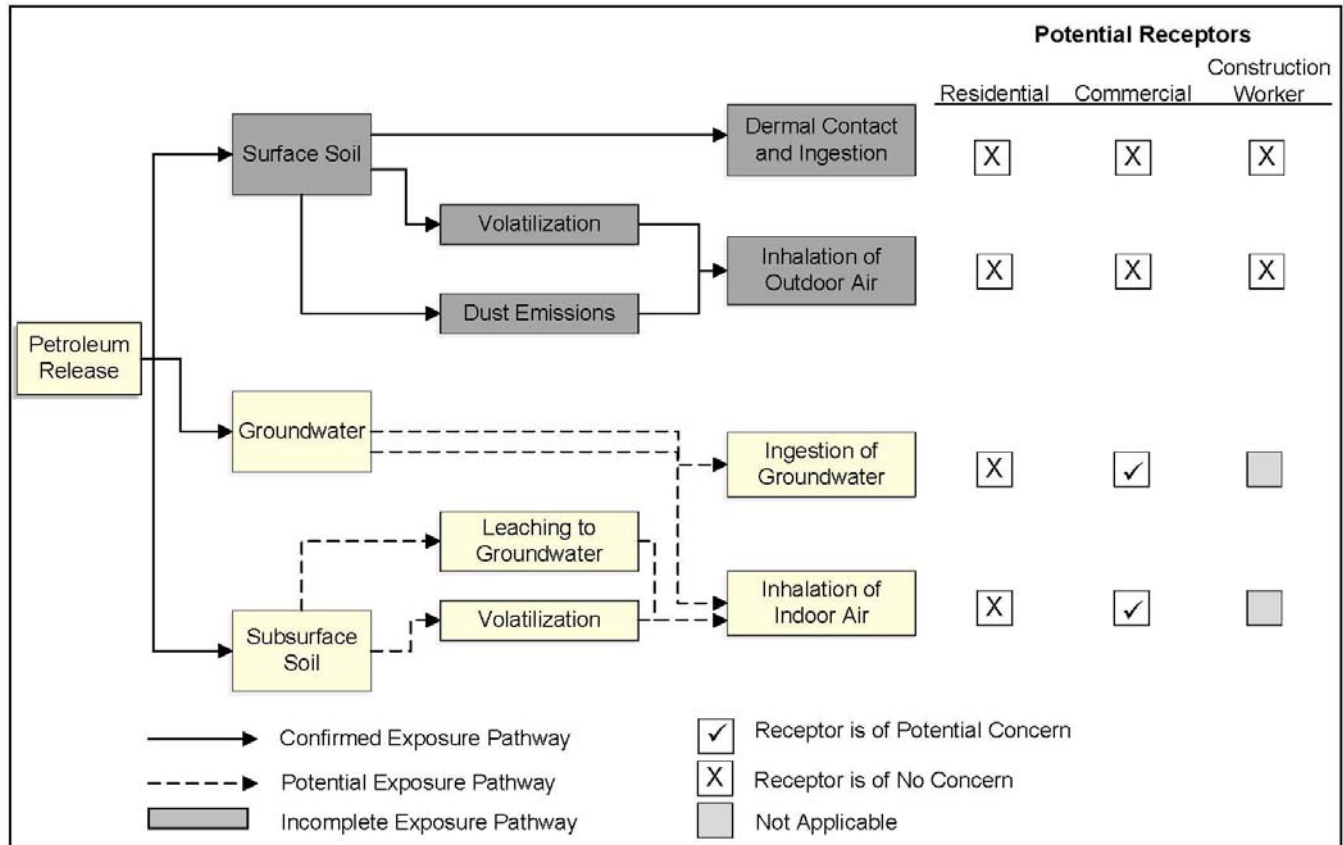
As data become available from site characterization, the CSM should be modified to reflect the current understanding of the conditions at the site.

#### CSM after Tank Removal

In this example, the tanks were removed from the former gas station site and visual staining of the soil was noted. Hydrocarbon impacted soil was not found until 10 feet below ground surface (bgs); however, the vertical depth and horizontal extent of the impacted soil and location of the water table are unknown. The site is located in a designated commercial/industrial area.

Because little information is known about the extent of the contamination and the hydrogeology of the site, the only pathways that can be eliminated at this point are those related to contact with surface soil. Also, because the site is in an industrial area, the residential receptors will not be considered. At this point, the CSM may be updated to look like Figure 4.

Figure 4 - CSM Example – After Tank Removal



### After Initial Site Investigation

After initial site investigation and collection of soil samples, the source was delineated both vertically and horizontally. The impacted soil was found to extend to groundwater. Groundwater samples were collected, and the results show concentrations in excess of the California Maximum Contaminant Levels (MCLs). This information does not change the CSM; therefore, the current CSM is the one shown in Figure 4.

During risk management, each of these pathways will be evaluated in more detail and appropriate management options identified. For example, since the groundwater is already impacted, the concentrations in the unsaturated zone may not contribute to human health risk; therefore, remediation of the soil may not be necessary. Other considerations, such as mobility limits, will need to be evaluated as discussed in [Risk Evaluation and Risk Management](#).

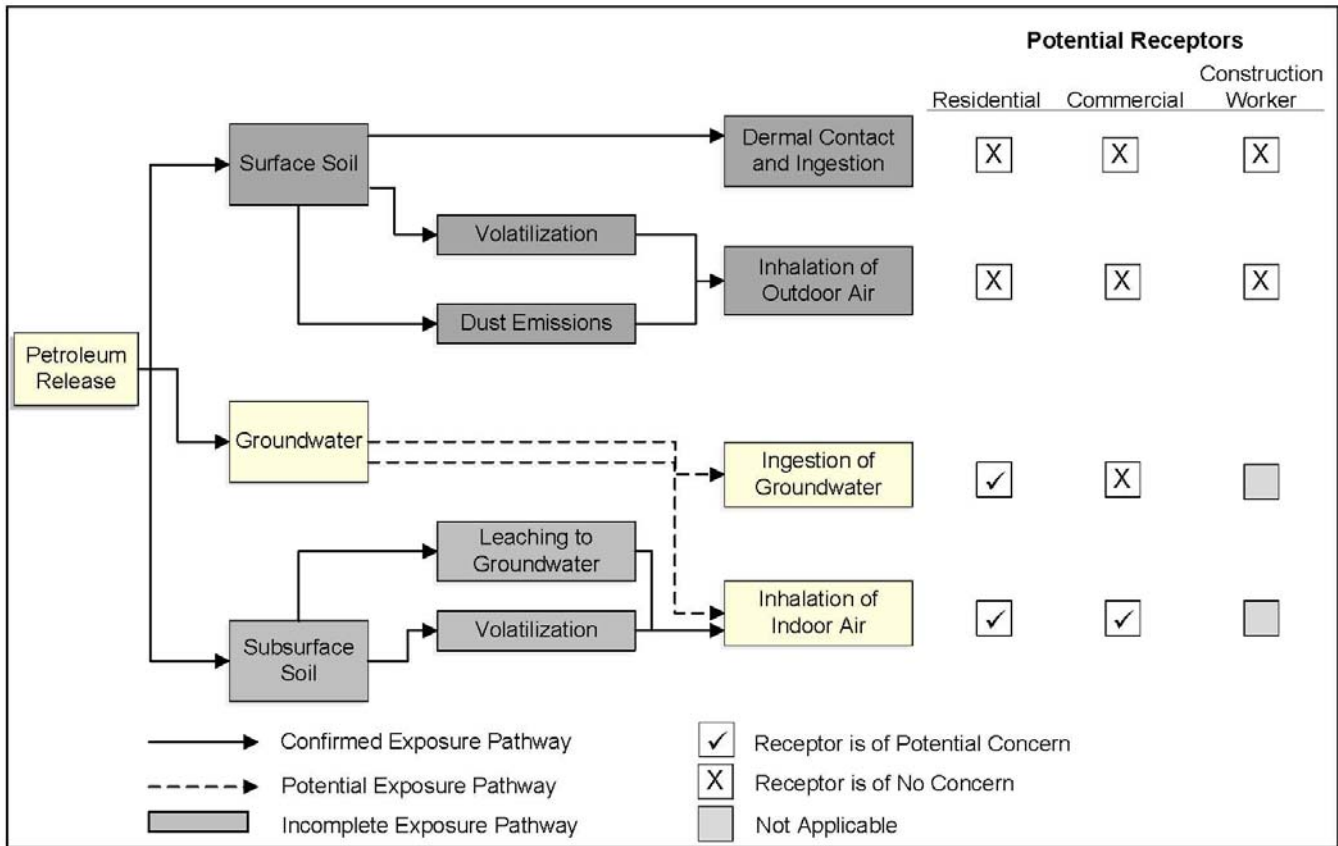
### Sites Remaining in Operation

For a gas station that will continue to operate, impacted soil is usually covered with asphalt or concrete. This eliminates the potential for direct contact with soil and the potential for volatile or dust emissions. If the soil concentrations are below mobility limits and the contamination has not reached groundwater (or the highest anticipated depth to groundwater), the potential for leaching to groundwater may be eliminated because there is little to no infiltration. In that case, there would be no complete exposure pathways at the site. (Note: as described in the "Receptors" section, if the site is an operating service station and air quality is being monitored for the worker, then the vapor intrusion pathway may not need to be considered.) Consideration should be given as to whether the land use at this location will change such that infiltration through the site may occur (irrigated landscaping or infiltration of rain water), leading to increased probability of mobilizing residual contaminants.

Any trenching or construction work that would be performed while the station is operating will require that the construction workers have an adequate health and safety plan, and therefore these exposures do not need to be included in the CSM.

For operating sites where groundwater has been impacted above WQOs, potential impacts to off-site receptors may need to be evaluated for the groundwater ingestion pathway and volatilization of contaminants to indoor air pathway. In that case, the CSM will look somewhat like the diagram shown in Figure 5.

Figure 5 - CSM Example – Operating Service Stations



Conceptual Site Model

However, if no one on- or off-site is currently using the impacted groundwater, the groundwater ingestion pathway would not be complete. Consideration will need to be given as to whether WQOs will be met in the future before this groundwater could be used beneficially.

### Sites Undergoing Redevelopment

A gas station that is in the process of being redeveloped for a different use must be evaluated consistent with the expected future land use. In these cases, direct contact with surface soils may be of concern as well as any of the other three common exposure pathways. In this case the CSM will look something like that shown in the initial CSM when no data was available (Figure 3). The [Risk Evaluation and Risk Management](#) chapter provides detailed options for addressing all four pathways.

### References

Interstate Technology & Regulatory Council (ITRC). 2007. Vapor Intrusion Pathway: A Practical Guideline. VI-1. Washington, D.C.: Interstate Technology & Regulatory Council, Vapor Intrusion Team. January. More information at: <http://www.itrcweb.org>

Merriam-Webster. 2010. Merriam-Webster On-Line Dictionary. <http://www.merriam-webster.com/dictionary/model>. Accessed on 4/15/2010.

# Site Assessment

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## Scope of This Chapter

This chapter presents a summary of strategies, methodologies, and technologies used to assess releases from underground storage tanks (USTs), including strategies for assessment, pre-field work considerations, soil investigation, groundwater sampling, well construction and development, soil-vapor investigation, and a review of lessons learned from previous work at LUFT sites.

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**Legal.** Title 23 of the California Code of Regulations (CCR) defines site assessment requirements (Division 3, Chapter 16, Article 11).

The term “site assessment” can have different meanings depending on how it is used. More generally, the site-assessment phase of a LUFT cleanup encompasses the activities necessary to create and validate the conceptual site model (CSM) before undertaking active remediation. More specifically, this chapter focuses on field activities to collect data about actual site conditions; these data will fill data gaps and validate the CSM.

The main intent of site assessment is to define the type of contaminants, the concentration of the contaminants, and to the degree appropriate the lateral and vertical extent of the contaminants.

## Hydrogeology and the CSM

Site geology, in most cases sub-surface stratigraphy, in part controls groundwater flow and pollutant transport, i.e., the site hydrogeology. A CSM predicts pollutant transport, largely based on geologic inference and interpretation. A competent California Professional Geologist or Certified Hydrogeologist should therefore closely supervise related data acquisition and interpretation. Direct methods of preliminary data acquisition generally include the following:

- Borings, e.g., auger, direct push, rotary, sonic
- Trenches, e.g., UST excavations
- Cone Penetration Testing (CPT)
- Grab groundwater sampling from temporary points, Membrane Interface Probes (MIPs), and Laser Induced Fluorescence (LIF)

Indirect methods (remote sensing), while less common at typical LUFT sites, can include:

- Surface geophysics, e.g., Ground Penetrating Radar (GPR), seismic refraction/seismic reflection, electromagnetic induction (EM), line tracing
- Borehole geophysics, i.e., electrical, acoustic, and nuclear logs (both active and passive)

The application of these indirect methods is discussed in the [Pre-Field Work Consideration](#) section of this chapter.

Data, primarily from soil borings, support the design of groundwater monitoring wells. Under appropriate professional supervision, drillers install monitoring wells with slotted casing intervals open to relevant permeable units of native formation. Follow-up static water level measurements, groundwater samples, and aquifer tests become the primary basis for interpretation of groundwater flow and pollutant transport. Monitoring wells must isolate relevant permeable units to avoid common pitfalls: false hydraulic gradients and cross-contamination (i.e., creating a vertical conduit between discrete polluted and unpolluted permeable units). The CSM, in part a prediction of well-to-well correlation, should therefore help defend monitoring well constructions. Technologies to install monitoring wells, along with piezometers and temporary well-points, are presented later in this chapter.

Based on boring and monitoring well data, the CSM should predict groundwater flow and pollutant transport in relevant perched, unconfined, semi-confined, and confined permeable units, and identify thicknesses and lateral extents of key aquitards. For further definitions, see Fetter 2000.

Along with site data, the CSM should incorporate identified recharge and discharge areas, hydrographic data from nearby sites, and regional permeability trends.

# Site Assessment

## Site Assessment Strategies



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### Initial Approach to Site Assessment

The investigation approach can dramatically affect cleanup strategies, project costs, and schedule. Key parameters typically include pollutant distributions in soil, soil gas, and groundwater, their biodegradation rates, and their transport rates from the source toward receptors. Because investigators must extrapolate between borings and monitoring wells to estimate key parameters, and drilling mobilizations are major cost drivers, an *effective* investigation approach is critical.

#### “Step-out” vs. “Step-in”

A “step-out” site-assessment approach employs soil borings and monitoring wells at or near the source to estimate maximum pollutant concentrations, and “steps out” drilling locations away from the source to assess the extent of constituents of concern (COCs) along predicted pollutant transport directions. This approach, often the least expensive, is amenable to inactive sites with unlimited drilling access, but is not always practically feasible. For example, typical sources at active sites such as fuel dispenser islands, piping, and USTs, are not safely accessible. Also, there are numerous sites which, despite the existence of monitoring wells, have data gaps; for example, unexplained discrepancies between apparent groundwater flow directions and pollutant distributions. In these cases, an investigator must often use a “step-in” approach.

A step-in strategy begins with borings and monitoring wells in areas with relatively low pollutant concentrations, and then investigates inward, toward the suspected source, along predicted permeability channels. For guidelines concerning where to begin a step-in approach, there is a discussion of typical plume length/ extent in the [Fate and Transport](#) chapter. Decisions can then be made about the need for additional precautions to protect previously uncontaminated zones.

**Note.** Advancing borings in or near the source area may have unintended negative consequences. Drilling through a confining layer or highly impacted soils can produce vertical conduits or drag contamination downward. In addition, drilling near USTs and piping increases the chances of encountering these underground objects during drilling and causing additional releases. Consequently, drilling in or near source areas should be done with caution.

### Multiple-Phase vs. Single-Phase Investigations

Prior to initiating field activities, it should be determined whether the work will occur in a single or in multiple phase(s). This decision is usually based on how quickly data gaps in the CSM need to be filled, the regulatory approval process, and the reimbursement approval process (for sites being reimbursed by the Fund).

In a multiple-phase investigation, the data are collected and evaluated in incremental steps. Further investigative work is determined by the data collected. Generally, as more information becomes available for a site, the site CSM is revised and used to plan the next phase of the investigation.

A single-phase investigation (also known as expedited site assessment) compresses the data-collection and CSM revision process into one mobilization of resources and equipment. Generally, this approach is used at sites that need a rapid turn-around time. While a single phase is faster, it may also be much more complex and require a dynamic work plan (discussed in the [Work Plan](#) chapter), *in-situ* data analysis, experienced personnel onsite with the discretion to make decisions regarding the field data and the scope of work, agreement on approach from all stakeholders, *and* a method for stakeholders to make decisions regarding in-field data.

Some pros and cons of multiple-phase and single-phase investigations are provided in Table 6.

**Table 6 - Pros and Cons of Multiple- and Single-Phase Investigations**

	Pros	Cons
<b>Multiple-Phase Investigation</b>	<ul style="list-style-type: none"> <li>• May allow for better planning by allowing for continuous update of the CSM and evaluation of data in incremental steps.</li> <li>• Allows for timely cost-management strategies to be developed. Long-term costs may decrease due to better management strategies.</li> <li>• May allow for early involvement of remediation engineers to evaluate data needed for assessment of remediation options.</li> <li>• May allow for better communication between lead agency and responsible party (RP)/ consultants.</li> </ul>	<ul style="list-style-type: none"> <li>• Time requirements for site assessment may increase, thus increasing long-term disruptions to the site due to assessment operations.</li> <li>• Regular site operations and businesses may be affected over longer periods.</li> <li>• Potential development opportunities for the site may be delayed.</li> <li>• The potential for completion of pathways to receptors increases due to lengthened site-assessment time.</li> <li>• Long-term costs could potentially increase due to more numerous mobilizations to site.</li> </ul>
<b>Single-Phase Investigation</b>	<ul style="list-style-type: none"> <li>• Site assessment may be completed more rapidly, potentially resulting in fewer long-term disruptions to the site.</li> <li>• Long-term site-assessment costs may decrease, due to lower numbers of mobilizations to the site and fewer long-term site disruptions.</li> <li>• Impacts may be remediated more rapidly, possibly minimizing potential for completion of pathways to receptors.</li> <li>• Site may be developed for new uses more rapidly.</li> </ul>	<ul style="list-style-type: none"> <li>• The possibility of incomplete planning increases due to unknown details about the site and an incomplete CSM, thus potentially increasing costs resulting from performing unnecessary work.</li> <li>• The planned field work may not provide a complete set of analytical data needed to fully characterize the site.</li> <li>• Incomplete data set may result in a multiple-phase investigation.</li> </ul>

### **Areal Extent of Petroleum Hydrocarbons: Radial Sampling Pattern vs. Linear Transects**

When determining the areal extent of contamination, it has been common practice to locate soil borings and monitoring wells at roughly equal distances from the source, stepping out until the edge of the plume is determined. This can work well at sites with inconsistent groundwater flow directions, complex permeability trends due to stratigraphy, and many obstacles such as buildings, utilities, etc.

At sites with relatively consistent groundwater flow directions along relevant permeable units, this radial pattern becomes elongated in one direction, and the resulting random spatial pattern complicates the analysis of the pollutant plume over time. A linear transect of wells perpendicular to the long axis of the plume allows a more consistent time series analysis (for example, a mass flux analysis).

### **Screening Methods**

Various screening methods can be used as an approach to initial site assessment. Example tools are the Rapid Optical Screening Tool (ROST), LIF, MIP, electron acceptor mapping, soil-gas surveys and soil headspace screening. To optimize the use of screening tools, work plans should provide for sufficient contingency borings to reduce overall project costs. Sufficient boring locations can help define source zones and guide investigations to define pollutant extent reasonably well in a single mobilization.

#### ***ROST, LIF, or MIP Coupled with CPT***

Groundwater flow directions and plume extent are usually not known at the time of the first assessment. Screening technologies such as ROST, LIF, or MIP coupled with CPT to define stratigraphy, locate free-phase hydrocarbons, and minimize the potential for cross-contamination (a small-diameter hole that can be filled with bentonite slurry from total depth to surface) can be used.

**Electron Acceptor Mapping**

Preliminary groundwater sampling for electron acceptors can also serve as a screening tool. For example, measurements of dissolved oxygen, carbon dioxide, methane, reduction potential (Eh), pH, iron II, sulfate, nitrate, and alkalinity, as well as petroleum analyses, can reveal zones of relatively slower, anaerobic, and/or faster, facultative and aerobic, bacterial pollutant decay. Investigators can construct preliminary maps of these parameters in the field to help select further drilling locations. See (for example) Chapelle, et. al 2000.

**Soil-Vapor Investigations**

Soil-vapor investigations can economically screen source-area locations and evaluate the relative size of an impacted area. Soil-vapor samples, both passive and active, can show the extent of mobile chemicals in the vadose zone, and infer their distribution in underlying groundwater. Cost per sample is typically low relative to deeper borings and monitoring wells.

After the soil-vapor evaluation phase is completed, soil borings may be installed to further evaluate chemical impacts using the soil-vapor data as a guide.

**Soil Headspace Screening**

This method can be used to economically delineate the lateral and vertical extent of LNAPL smear zones if soil borings are advanced. It is easy to perform (put soil samples into a zip lock bag for a specified time period and then measure the volatilized hydrocarbons in the bag using a PID) and provides real-time information in the field.

**Background Sampling Strategy**

Background sampling is often performed at chemical release sites to determine the naturally occurring background levels of specific constituents (such as metals); however, at most petroleum release sites these constituents are typically not of concern and background sampling is not necessary. If other pollutant sources (e.g., other LUFT sites, dry cleaners, etc.) are within relevant distance, upgradient groundwater samples can help determine their relative contribution to a LUFT site. GeoTracker and EnviroStor can help to locate nearby release sites.

# Site Assessment

## Pre-Field Work Considerations



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There are several things to consider prior to beginning field work, such as preparing a work plan, acquiring appropriate permits, etc. The following is a discussion of important pre-field considerations. Please note that this is not intended to be all-inclusive, as each LUFT site is unique and has unique requirements. It is important for RPs and consultants to work with the regulatory agency overseeing the site assessment to ensure that pre-field considerations have been addressed prior to mobilization for field work.

### Work Plan

Submittal of a work plan is required prior to conducting field activities associated with a LUFT site assessment as discussed in the [Work Plan](#) chapter of this Manual.

### Site-Specific Regulatory Requirements and Permits

It is important to understand the regulatory requirements for assessing LUFT sites. Applicable regulatory requirements may include federal, specific state, county, and municipal guidelines for delineating soil and groundwater impacts, as well as expected or potential cleanup goals. Soil and groundwater delineation objectives and cleanup guidelines are often presented in the guidance documents from overseeing agencies. The lead regulatory agency oversees activities and reports associated with the site, including work plans, field work, reporting, corrective action planning, GeoTracker compliance, and others.

Worker and community health and safety are an important component of site assessment; they are discussed in the [Health and Safety](#) chapter.

Permits may be required prior to site assessment (and cleanup phases); each local agency has its own specific permitting requirements. The RP is required to obtain the proper permits in order to perform work. Permits may be required for advancing borings (including CPT points) and are generally required for constructing and destroying monitoring wells. Depending on the location of the site, permits are typically obtained from either county or municipal agencies, such as environmental health/fire departments, water districts, planning departments, and/or building departments.

If work is being completed in public rights-of-way (sidewalks areas, roads, etc.), an encroachment permit is often required. If assessment is needed at an off-site location, or if the subject site is no longer owned by the RP, the RP (or RP's agent) will likely need to obtain an access agreement with the owner(s) of the property where work is to be conducted.

As part of the well or boring permit process, many regulatory agencies require the property owner to sign forms indicating that the property owner agrees to have the assessment performed. If he or she refuses to grant reasonable access, the regulatory agency may require the property owner to conduct the required work at his/her own expense. This process can be very time-consuming, and should be factored into the schedule for work completion.

### Regulatory Oversight

An inspector from the lead regulatory agency or local oversight agency, which has issued a specific permit, has the authority to be present during site work, unless prior approval to proceed without an inspector onsite has been obtained. Each agency may have its own specific notification requirements, including notification, or lack thereof, for routine monitoring or maintenance events. The agency has the regulatory authority to reject analytical or field results obtained during field work if the proper inspection arrangements have not been made and there is a reasonable suspicion that the data are not valid.

It is recommended, and may in fact be required by some regulatory agencies, that the RP and consultant contact the regulatory agency to schedule an inspection a minimum of three business days (or other agreed-upon interval among RP, consultant, and regulatory agency) before proposed site work begins. If either the date or the field-work schedule is changed from a previously agreed-upon time, whichever party first becomes aware of the change notifies the other parties in the manner previously agreed upon (email, fax, etc.).

# Utility Location and Clearance

California requires that the RP mark any underground subsurface work locations (e.g., drilling locations, excavation locations, trench locations, etc.) in white paint and contact Underground Service Alert North in northern California (<http://digalert.org>) or DigAlert in southern California (<http://www.call811.com>) at least 48 hours in advance of any work to acquire a ticket number. USA North/DigAlert will notify listed underground utility owners (members) with facilities near the investigative area. Members then send personnel to the site to locate the underground utility locations and/or clear the marked work locations within 24 inches of the marked location. USA can be contacted at (800) 227-2600 throughout California.

**Important!** The locations of underground utilities need to be identified before any drilling work or excavation work is performed at a LUFT site. Encountering underground utilities during drilling and excavation operations can be extremely dangerous, life threatening, and costly.

The RP can request a meeting with the different listed members to discuss the project and walk the site. The RP and/or the RP's agents should consider hand augering, pot-holing, or air-knifing proposed drilling locations to a depth of 3 to 6 feet below ground surface (bgs) before drilling operations begin. The law requires that the site be excavated to a point of "no conflict" 24 inches on either side of the underground utility/facility, so the exact locations can be known before using power equipment.

USA members are not responsible for clearing underground utility corridors on privately owned land. Consequently, the RP should review available as-built maps for underground utility locations. In addition, the RP should consider sub-contracting a private and licensed underground utility locator.

**Further Reading.** Further information on Dig Alert and the law can be reviewed at [www.digalert.org/index.asp](http://www.digalert.org/index.asp), [www.call811.com](http://www.call811.com), or <http://www.usanorth.org> (for Northern California).

## Geophysical Surveys for Utilities and Other Underground Features

Surface geophysical surveys are generally conducted to better understand the location of USTs and associated piping at LUFT sites, but may also be performed to investigate the location of drums, other utilities, building foundations, vaults, etc. Additionally, geophysical data can be used to identify former excavations. The primary intent of using geophysical data during site assessment is to gather as much information about subsurface objects and conditions as possible without disturbing the surface or conducting expensive exploratory excavation or trenching. Generally, available site as-built construction drawings and other documents should first be reviewed to evaluate UST and associated utility locations before conducting geophysical surveys. Geophysical surveys can be invaluable in directing site assessments; however, the accuracy of geophysical data is highly dependent on site conditions and the skill and experience of the geophysicist conducting the survey (USEPA 1997, Department of Toxic Substances Control [DTSC] 1994).

Some of the geophysical survey methods used in site investigations are discussed below; Table 7 provides a list of pros and cons for each method.

- **GPR.** The process of transmitting electromagnetic energy into the ground and measuring the time it takes for that energy to be reflected back to the receiving unit. By measuring and logging the timing and strength of the returning signal, an image of the subsurface, including foreign objects, such as USTs, vaults, or piping can be created.
- **Seismic Reflection/Refraction.** Seismic data are similar to GPR, in that seismic reflection/ refraction transmits acoustic waves into the subsurface, and measures both the strength of the returned signal and the time required for waves to be reflected. Seismic reflection and refraction can be very useful in identifying former excavations, and in aiding the delineation of the subsurface geology of a site.
- **Electromagnetic Induction (EM).** EM is an advanced form of metal detection. By using an electric coil to create a magnetic field, the EM equipment can measure secondary magnetic fields created from buried ferrous metal objects, such as USTs and metal drums.
- **Line Tracing.** By inducing or impressing a signal into an exposed or known utility or piping (such as a metal water pipe or vent line), a receiver can be used to trace the subsurface location of the line. Additionally, non-metallic lines, such as sewer pipes, can be traced by inserting a signal antenna connected to a transmitter into the length of the pipe and

tracing it with the receiver. Line tracing is extremely valuable for health and safety during site assessment activities, by identifying live utilities in drilling and excavation locations.



**Table 7 - Pros and Cons of Geophysical Survey Methods**

	Pros	Cons
<b>GPR Imaging</b>	<ul style="list-style-type: none"> <li>GPR data are relatively inexpensive to gather.</li> <li>Gathering GPR data is non-destructive.</li> <li>GPR can be used to identify metallic and non-metallic objects, as well as excavations.</li> <li>GPR can be used on a multitude of sites with varying ground cover, including soil, asphalt, and concrete.</li> </ul>	<ul style="list-style-type: none"> <li>GPR equipment is sensitive and can receive interference from structures, such as walls and ceilings, or from large equipment.</li> <li>GPR may not be effective in collecting data below reinforced concrete.</li> <li>Depending on subsurface soils, GPR may have a relatively low depth range. Moist clays restrict the GPR image depth more than dry sands do.</li> </ul>
<b>EM</b>	<ul style="list-style-type: none"> <li>EM data are relatively inexpensive to gather.</li> <li>Gathering EM data is non-destructive.</li> <li>EM can be used on a multitude of sites with varying ground cover, including soil, asphalt, and concrete.</li> <li>Good lateral resolution.</li> </ul>	<ul style="list-style-type: none"> <li>EM equipment is sensitive and can receive interference from vehicles, metal fences, metal structures, and reinforced concrete.</li> <li>EM will only identify metallic objects; it will not identify fiberglass or PVC.</li> <li>Poor vertical resolution.</li> </ul>
<b>Line Tracing</b>	<ul style="list-style-type: none"> <li>Line tracing data are relatively inexpensive to gather.</li> <li>Gathering line tracing data is non-destructive.</li> <li>Line tracing can be used on a multitude of sites with varying ground cover, including soil, asphalt, and concrete.</li> </ul>	<ul style="list-style-type: none"> <li>Line tracing usually requires a starting point. This can be an exposed utility or vent line, or a known subsurface utility location.</li> </ul>
<b>Seismic Reflection/Refraction</b>	<ul style="list-style-type: none"> <li>Gathering data is non-destructive.</li> <li>Good for large area reconnaissance.</li> <li>Good vertical and lateral resolution.</li> </ul>	<ul style="list-style-type: none"> <li>Susceptible to vibration noise.</li> <li>Field operations more complex.</li> </ul>



# Site Assessment

## Soil Investigation



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A soil investigation at a LUFT site is conducted to characterize the source and the extent of a release. It also serves to establish the severity of the release and the impacts to receptors by providing concentrations of COCs. There are several methods available for investigating and collecting soil samples, as discussed in this section.

### Laboratory Analysis and Methods

The laboratory analyses and methods for COCs in soil samples at LUFT sites are discussed in the [Laboratory Analysis and Methods](#) chapter of this Manual. In addition, the Analytical chapter sets forth recommended testing for forensic purposes for soil and free-product samples.

### Selecting the Proper Soil Investigation Method

A petroleum release can occur aboveground (spills and dispenser leaks) or in the subsurface (USTs and piping) at a LUFT site. In order to characterize the release and further develop the CSM, the area of impact needs to be evaluated using the appropriate investigation method.

#### Hand Auger

For shallow soil investigations (about 5 to 8 feet bgs or less), hand augering may be adequate. Soil samples can be collected using either a specialized bit or a hand-drive sampler loaded with brass tubes. Hand augers are also routinely used to clear drilling locations of underground obstructions.

#### Test Pit – Excavator

Test pits are frequently used to investigate shallow soil conditions and stratigraphy. The pit is usually dug using a backhoe or excavator; the size of the equipment used is dependent on the depth of the test pit. Test pits are particularly useful for obtaining a “bigger picture” cross-sectional view of stratigraphic contacts and the location of soil staining or the occurrence of light non-aqueous phase liquid (LNAPL), as compared to borings. The sidewalls of test pits are usually logged by drawing a cross-sectional view and identifying:

- Soil types and the depth of contacts
- Observations of fill
- Observation of staining
- Important natural or man-made features
- The water table

Soil samples can be collected from test pits either by driving brass tubes into the sidewalls or bottom of the pit, or (in the case of deep pits) samples are usually collected by driving a tube into the soil from the excavator bucket. Test pits are backfilled either with the excavated soil or imported fill in accordance with regulatory requirements. Compaction of the backfilled pit is also accomplished per regulatory requirements.

#### Drilling

There are several drilling technologies used to investigate the impacted area. Selecting the proper drilling method requires balancing the objectives for the field work. Important criteria to consider include:

- Depth of the soil investigation
- Soil type
- Sampling needs for soil and groundwater
- Access constraints
- Cross-contamination concerns
- Whether or not a groundwater well will be placed within the boring.

Consideration of the geology and hydrogeology at the site is important when selecting a drilling method. The depth to which the boring has to be drilled in order to access the impact area and/or to install a well to monitor a selected water-bearing zone may exceed the practical depths of a particular drilling technique. In addition, certain saturated geologic materials, under high hydrostatic pressures, may either:

- 1) Impose increased frictional resistance (i.e., expanding clays), which limits the practical depths reached by some drilling methods.
- 2) Create unstable borehole conditions (e.g., heaving sands), which may preclude the use of some drilling methods for installation of the monitoring well.

# Site Assessment

## Soil Investigation:

### Drilling Methods



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The following is a discussion of various soil drilling methods. It is intended to provide insight as to when and under which conditions the method(s) could be implemented. The discussion describes methods typically used at LUFT sites; it's not intended to be a comprehensive description of drilling methods.

#### Continuous Core vs. Discrete-Depth Sampling

The investigator must decide whether continuous core or multiple discrete-depth samples will be collected to evaluate site stratigraphy. Continuous logs of the subsurface are particularly valuable because they can be used to produce accurate hydrogeological cross-sections and help to develop a three-dimensional CSM. It has been well established that the historic practice of collecting soil samples for geological logging only at 5-foot intervals results in an inadequate, incomplete, and often inaccurate understanding of site stratigraphy and migration pathways. Because of this, the interval sampling approach is not recommended unless the site stratigraphy has already been established using continuous cores. The additional cost of continuous coring is minor relative to the value of the information gained.

Continuous cores can be collected with direct-push technologies (DPTs), hollow-stem augers (5-foot split barrel), mud-rotary drilling (wireline system), or sonic drilling. It is recommended that continuous cores be collected at as many locations as necessary to characterize the site stratigraphy and the lateral and vertical distribution of petroleum at the site.

#### Common Methods Used to Advance a Borehole

Various methods used to advance a borehole are discussed in subsequent sections; a summary table presenting some pros and cons of each of these methods is provided in Table 8; and Figure 6 presents some of the common drilling methods.

Whichever method is selected, great care must be taken when advancing borings or installing wells through LNAPL source zones. In these cases, special measures must be taken (e.g., conductor casing or "dual tube" methods) to reduce the potential for cross-contamination (drag-down) during borehole advancement and sampling.

#### Direct Push Technology (DPT)

DPTs, commonly used for preliminary investigations of LUFT sites, are a category of continuous-core equipment that drives steel rods into the ground using a combination of a hydraulic ram and a percussive hammer. Direct-push rigs (for example, Geoprobe®) are most commonly used for the collection of soil and grab groundwater samples. CPT and MIP rigs are also considered DPTs. DPTs allow cost-effective, rapid sampling and data collection in unconsolidated soils and sediments.

A variety of equipment is available, particularly in the type of attachments used at the end of rods to collect samples and data. Some examples of tools that can be deployed using DPT include:

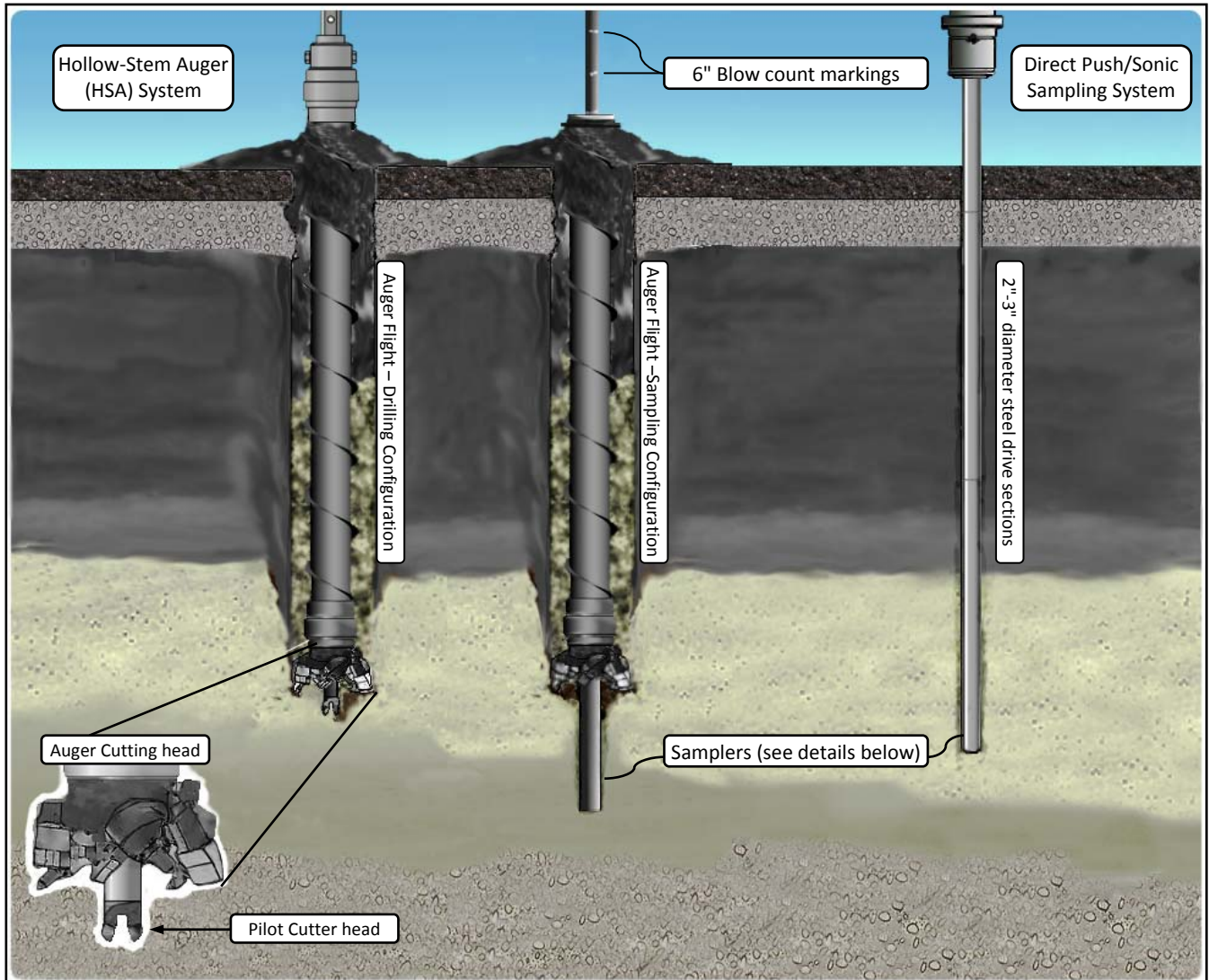
- Hydropunch-type samplers for collecting depth-discrete groundwater samples. (Discrete samples are those collected from a single distinct location).
- Macrocores and large-bore samplers for collecting both continuous and depth-discrete soil samples.
- In-situ, direct-sensing instruments such as Cone Penetrometers, the MIP, and LIF tools.
- Soil-gas samplers.

These attachments can collect soil, soil-gas, or groundwater samples, perform *in-situ* analysis of contaminants, or collect geophysical data that are continuously logged as the DPT rods are advanced. As discussed above, the continuous logs of subsurface conditions are particularly valuable in site interpretation.

Direct-push rigs come in a variety of configurations, from truck-mounted systems to all-terrain track rigs and small dolly-mounted rams, and in single- and dual-tube configurations. In California, direct-push rigs can generally reach depths of 50 to 100 feet bgs in unconsolidated finer-grained soils, although CPT rigs may be able to reach 150 feet bgs in some conditions.

As a general rule, the larger and heavier the rig, the greater the depth it can achieve. For indoor work, small dolly-mounted rams can operate in small spaces, but need to be anchored to a concrete floor. In areas with cobbles, gravels, and hard-packed sediments, DPT is not a feasible option. The most appropriate uses of DPT are for shallow investigations in soft sediments, for limited access (indoor) applications, and in sensitive areas to minimize surface disturbance.

Figure 6 – Common Drilling Methods and Soil Sampling Systems



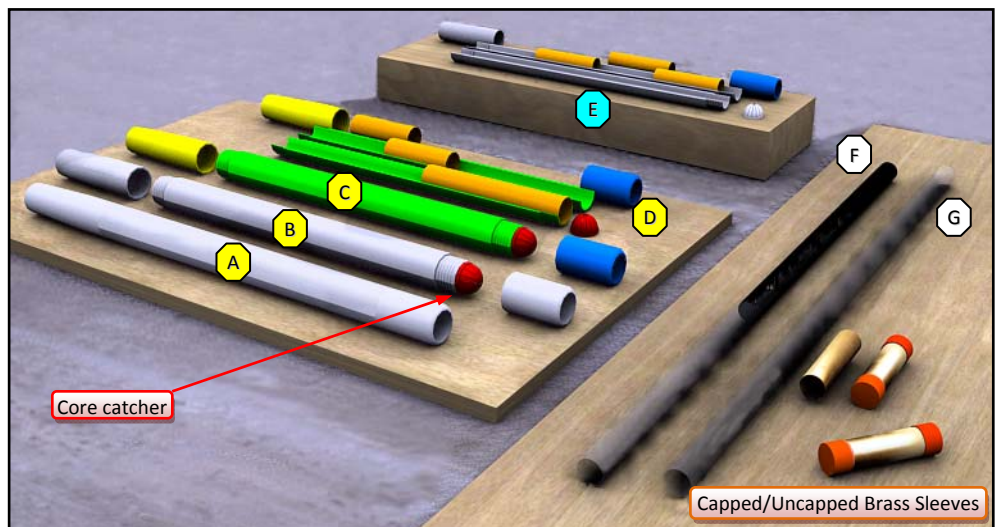
**24-inch Split-Spoon Samplers (4 illustrated)**

- A** Shown assembled (36"-42" total length)
- B** Partially disassembled
- C** Partially disassembled and colored by component
- D** Colored and fully disassembled with brass sample sleeves

**Direct-push Sampler Acetate Sleeves, (used) 4' total length × 2" diameter - (2 illustrated)**

- F** 24" sample recovery hydrocarbon-stained soil
- G** Sleeve with no recovery

**E Standard Penetration (SPT) Sampler (1.5-inch dia.) with brass sleeves**



## Hollow Stem Auger (HSA)

HSA is a drilling method commonly used at LUFT sites; it uses continuous-flight augers to penetrate the soil. As the augers are rotated, soil cuttings are brought to the ground surface via auger flights. A core barrel is often inserted inside the augers. Samples from discrete depths are collected during a Standard Penetration Test during which a split-barrel sampler, typically 2 feet in length, is hammer-driven into the native formation at selected depths. Alternatively, a continuous-coring barrel can be driven over the length of each auger, typically in 5-foot increments. Each sampling method allows a minimally disturbed sample of native formation. Sample disturbance can be controlled by close evaluation of core recovery during drilling. A variety of sampling tools can be used inside the hollow augers for soil and groundwater sampling and well construction.

Appropriate situations for HSA:

- Unconsolidated or partially consolidated lithologies, including gravels and cobbles.
- Maximum total depth capability up to 200 to 300 feet.
- Monitoring and/or remediation well installation.

## Rotary Drilling Methods

Relatively less common at LUFT sites, rotary drilling is the process of cutting a borehole in which the ground is cut or crushed by a rotating drill bit. Rotary drilling uses circulating fluids (e.g., mud, water, or air) to remove the drill cuttings and maintain an open hole as drilling progresses. Rotary drilling is not generally amenable to extensive intact native formation sampling; boring logs are generally via monitoring of cuttings and, in some cases, follow-up borehole geophysics. Rotary drilling methods can be used to depths of several thousand feet. They are fast and effective in many types of lithology, but produce more waste for disposal. Rotary rigs are also very large, and can be highly disruptive to site activities. In addition, on a cost-per-foot basis, rotary rigs can cost several times as much as HSA rigs.

### *Air Rotary/Air Rotary Casing Hammer*

Air rotary drilling forces air down the drill pipe and back up the borehole to remove the cuttings. If borehole stability or cross-contamination is a concern, then air rotary casing hammer (ARCH) can be used. ARCH is a drilling technique in which a hollow casing is driven at the same time the borehole is advanced by the rotary bit. The casing, which surrounds the drill pipe, is driven into the formation using a hammer which pounds the casing into the formation with a number of successive blows. This process seals off the borehole and minimizes cross-contamination.

### *Mud Rotary*

Mud rotary drilling uses a rotating drill bit at the end of a string of drill pipe. Drilling mud, a water-based drilling fluid, is pumped into the drill pipe and escapes through the bottom of the bit. The drilling fluid/mud is used to lubricate and cool the drilling bit, stabilize the borehole, and carry drill cuttings to the surface. When the drill cuttings are carried by the mud to the surface, they settle out of the mud in a settling pit. The mud is then re-circulated back into the borehole. Additional mud is added as the well gets deeper and mud is lost to the formation(s) being drilled (Nielsen 2006).

Borehole geophysics is typically cost-effective with mud rotary drilling methods. Common open-hole logging methods include spontaneous potential and electrical resistivity; these can accurately depict relevant aquifer and aquitard units without need of extensive intact soil samples.

Assuming that the mud is carefully monitored and a proper filter cake or mud cake is developed along the borehole wall, the mud rotary drilling method is used to reduce cross-contamination through an aquifer to a deeper zone. Like air rotary, mud rotary is costly as compared with HSA drilling, causes business and traffic flow disruption at typical LUFT sites, and is therefore seldom used. Although use of a mud rotary rig helps prevent cross-contamination when drilling through shallower parts of the saturated zone to a desired deeper location, other more cost-effective and less disruptive methods can be used to achieve the same goals.

**For Example,** use of conductor casing or a large-diameter auger flight to seal the borehole while installing a monitoring well at a particular depth interval is just as effective, and far less costly, than using a mud rotary drill rig.

## Sonic Drilling

Also relatively uncommon at typical LUFT sites, sonic drill rigs use an oscillator to produce high-frequency vibrations in the sonic rig drilling bit, which vibrates vertically as the bit is rotated downward. The process allows a sonic rig to drill through materials too hard for an HSA rig. The vibrations fluidize softer materials, and create fractures in hard soils and/or bedrock formations. The vibration frequency can be altered by the driller to adjust to different circumstances.

Sonic drilling is less cost-effective for shallow borings (less than 50 feet) because of the time and consequent cost of setup at each boring. Sonic drilling should be considered in situations where HSAs have difficulty, such as hard soils with gravels and cobbles or bedrock, deep drilling, and in instances where the shallow water-bearing zone should be isolated while the well is being installed in a deeper zone.



**Table 8 - Pros and Cons of Various Drilling Methods**

	Pros	Cons
<b>DPTs</b>	<ul style="list-style-type: none"> <li>• Reduced surface disturbance.</li> <li>• Minimal waste generation.</li> <li>• Small footprint for limited-access work.</li> <li>• Large variety of limited-access equipment options as compared with HSA.</li> <li>• Small borehole diameter well suited for soil-gas vapor well construction.</li> <li>• Ideal for one-time chemical injection points.</li> <li>• CPT rigs with LIF or MIP capability generate a detailed lithologic and contaminant log in real time without producing soil waste.</li> </ul>	<ul style="list-style-type: none"> <li>• Usually limited to drilling and shallow soil sample recovery in unconsolidated soil materials and very soft rock. Cannot penetrate most bedrock.</li> <li>• Difficult to impossible to penetrate cobbles, gravels, or hard-packed sediments.</li> <li>• May yield inconsistent core recovery.</li> <li>• Single tube has higher risk of cross-contamination.</li> <li>• Dual tube can decrease core recovery and consistency.</li> <li>• Cannot be used to collect many geotechnical samples.</li> <li>• Borings cannot be converted to conventionally sized (2-inch diameter or greater) monitoring and/or remediation wells.</li> <li>• CPT, MIP, and LIF data need to be confirmed by actual site data collected by traditional methods.</li> <li>• Proprietary soil gas samplers specifically designed to be used in a Direct Push boring do not consistently produce representative samples.</li> </ul>
<b>HSA</b>	<ul style="list-style-type: none"> <li>• Suitable for most exploratory boring and well-installation situations.</li> <li>• Ideal for collection of geotechnical samples.</li> <li>• Numerous soil sample tools of various diameters and lengths are available.</li> <li>• Cases upper part of boring to prevent caving and minimize cross-contamination.</li> <li>• Relatively quick and effective in poorly consolidated formations.</li> <li>• Does not introduce drilling fluids into the borehole.</li> <li>• Can install well screen and materials during auger removal.</li> <li>• Can be used as temporary casing for the installation of second, deeper-zone monitoring wells.</li> <li>• Grab groundwater samples can be collected with submersible pumps.</li> </ul>	<ul style="list-style-type: none"> <li>• Large surface disturbance as compared with DPT.</li> <li>• Greater waste generation as compared with DPT.</li> <li>• Fewer limited-access options than with DPT.</li> <li>• Limited diameter range for borings.</li> <li>• Not appropriate for bedrock drilling.</li> <li>• Large diameter borings poorly suited for soil-gas vapor well construction.</li> <li>• Difficulties caused by loose or flowing sands.</li> <li>• Smearing of clays may seal off water-bearing zone.</li> </ul>



**Table 8 - Pros and Cons of Various Drilling Methods (Continued)**

	Pros	Cons
<b>Air Rotary/ ARCH</b>	<ul style="list-style-type: none"> <li>• Can drill to great depths and through very hard materials such as bedrock.</li> <li>• Provides temporary casing to minimize cross-contamination and establish borehole stability for well construction (ARCH technique).</li> <li>• Does not introduce drilling fluid into borehole.</li> <li>• Provides identification of most water-bearing zones.</li> <li>• Can collect drive soil samples (ARCH technique).</li> </ul>	<ul style="list-style-type: none"> <li>• Seldom needed for most LUFT sites, as most LUFT sites are generally present at shallower depths in unconsolidated soils.</li> <li>• Cannot collect continuous core and samples occur as small particles that are difficult to interpret.</li> <li>• Air used in the drilling process can strip volatile organic compounds (VOCs) from the soils and groundwater, negating any value from sampling.</li> <li>• Large rigs can cause disruption to business, traffic flow at typical urban gas station settings; safety issues; air compressor and casing hammer are very noisy.</li> <li>• Not cost-effective compared with HSA rigs; use only if too deep or too hard for HSA to be used.</li> </ul>
<b>Mud Rotary</b>	<ul style="list-style-type: none"> <li>• Capable of deep drilling (&gt;1,000 feet).</li> <li>• Capable of penetrating bedrock.</li> <li>• Capable of continuous coring using wireline system.</li> </ul>	<ul style="list-style-type: none"> <li>• Well development (described later) is more problematic, since the mud needs to be removed.</li> <li>• Cannot discern the depth of the water table during drilling.</li> <li>• Costly compared with HSA drilling, even compared with conductor casing installed while using HSA.</li> <li>• Used drilling mud must be managed as a waste.</li> <li>• Large rigs and support equipment are disruptive to business and traffic flow at typical LUFT location and also pose a safety hazard.</li> </ul>
<b>Sonic Drilling</b>	<ul style="list-style-type: none"> <li>• No drilling fluid required.</li> <li>• Can drill through bedrock or cobbles.</li> <li>• Casing installed in boring during drilling, so no caving likely.</li> <li>• Capable of deep drilling (&gt;1,000 feet).</li> <li>• Continuous core collected in every boring.</li> <li>• Safe and rapid method.</li> <li>• Limited waste generated (very low quantity of drill cuttings).</li> <li>• Comparable in effectiveness to conductor casing in sealing shallower parts of the water-bearing zone while installing deeper monitoring wells.</li> <li>• Newer rigs come in a variety of sizes.</li> </ul>	<ul style="list-style-type: none"> <li>• Causes subsurface temperature to increase slightly; may cause some volatilization of contaminants.</li> <li>• Higher cost than HSA rig on a per-foot basis.</li> <li>• Rigs can be larger than many HSAs (but smaller than most rotary rigs).</li> </ul>

## Common Drilling Problems

Drilling refusal and heaving sands are two common issues encountered when drilling in the subsurface, as discussed below.

### Drilling Refusal

Drilling refusal occurs when the drill bit or split-spoon hammer cannot penetrate to the desired depth. This is usually because the material is too hard for the rig or method used. If refusal is encountered, the options are:

- Evaluate the data collected in terms of assessment goals, and confer with the regulator to determine whether sufficient information has been obtained such that, even though refusal has been met, no additional drilling is required.
- If refusal is met before sufficient information has been obtained to meet agency requirements, remobilization with another type of rig may be necessary.

### Heaving Sands

Heaving sands occur when the drill bit penetrates a well-graded, saturated sand layer that has sufficient hydraulic head to cause pressurized wet sands to “heave” up inside the auger, preventing the well from being set at the depth drilled to. Usually the solution to this is to re-drill to the desired depth, using a wooden plug in the bottom of the auger, which can be knocked out of the bottom with the split spoon when the well is ready to be set. The driller will have to work quickly to place the casing at the correct depth before the sands flow back in through the bottom of the auger. Alternatively, sonic- or mud-rotary drilling methods can be used, but these are more expensive than HSA drilling.

# Site Assessment

## Soil Investigation:

### Soil Sampling and Description



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#### Soil Sample Collection Methods

There are many guidance documents regarding the proper collection of soil samples. Standard soil sample collection procedures are discussed in (1) USEPA 1992 Guidance: *Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies* (this document also has a comprehensive treatment of sampling statistics); (2) USEPA Region 4 and the Science and Ecosystem Support Division (SESD) 2007 *Operating Procedure, Soil Sampling*; and (3) USEPA Region 9 Laboratory 1999 Guidance: *Field Sampling Guidance Document #1205, Soil Sampling*. It is important for the RP, the consultant, and the lead regulatory agency to agree on proper sampling protocols.

The implementation of EPA Method 5035 for preservation of soils collected for analysis of VOCs has necessitated slightly different soil-sampling methods than did historical protocols (DTSC 2004).

Historically, for DPT sampling, soil samples have been contained in an opaque or transparent sleeve that is not easily accessed for on-site evaluation. For DPT, use of clear liners is still recommended, with the top third of the tube removed for on-site core evaluation (lithologic description) and sample collection.

After sampling, the entire core section is visually examined. The on-site geologist can very quickly scan the core with a Photo-Ionization Detector (PID) to immediately evaluate the geology and whether the area has been impacted by petroleum. With this information, the on-site geologist can select the sample location. The sample is collected by removing the top 1 inch of soil, collecting the sample into the EPA Method 5035 preservation apparatus, and chilling as required.

For split-spoon samplers, non-VOC soil sampling is conducted using a split spoon lined with brass or stainless-steel sampling sleeves. Based on field data or a pre-determined sampling depth, the selected sleeve is sealed at both ends with Teflon film, capped, taped using non-VOC containing tape, and placed on ice in a cooler under chain-of-custody for transport to a State-certified laboratory for analysis. Samples should be delivered to the laboratory within 24 to 48 hours of collection, if possible, to limit the potential for analysis outside of method holding times.

When sampling with continuous-core split spoon samplers (e.g., 5-foot barrel), the core barrel is opened, the sample location is selected, and a brass tube is driven into the soil core. The tube is sealed, capped, taped, and chilled as described above. With the introduction of EPA Method 5035, sample sleeves are no longer necessary, as the sample is immediately preserved onsite. In fact, the brass sample tubes in a split-spoon sampler make the Method 5035 protocol more difficult without offering an advantage in terms of preserving VOCs. Therefore, collection of split-spoon samples (2.5-inch inside diameter) is easier without the brass sample tubes.

For continuous-core DPT sampling, non-VOC samples typically use an acetate sleeve. In DPT sampling, a geologist determines where samples are to be collected based on the data in the field, unlike other methods, where samples are collected at pre-determined depths. The acetate sleeve is cut, sealed, and capped.

After collecting the sample, the sample cylinders containing media for non-VOC analysis and VOC screening are confirmed as being full, capped, sealed with inert tape, and accurately labeled, and are then chilled as quickly as possible to minimize volatilization and possible loss of analytes.

**Note.** Samples are not to be sealed with duct or electrical tape, as the adhesive on these products may contaminate the sample with toluene.

#### Soil Description/Logging

At LUFT sites, the primary goals of boring logs are to support monitoring well design and borehole-to-borehole correlation. Descriptions should assist filter pack and well screen design, and minimize risk of cross-contamination during monitoring

well installation. Descriptions should be sufficient to extrapolate subsurface geology between borings and support predictions beyond the investigation area. It is also important that logging activities be within project cost constraints.

**Important!** Evaluation of site-assessment data is highly dependent upon subsurface geologic conditions; therefore, it is extremely important that reports of site-assessment activities contain accurate boring logs, so that future review and reconstruction of any evaluations made or conclusions drawn will be possible.

Historically, LUFT investigations have relied solely on the Unified Soil Classification System (USCS), after American Society for Testing and Materials (ASTM) D-2488; see Howard, A.K. (1986). The USCS/ASTM system, originally designed for geotechnical investigations, is useful for fine-grained soils with limited matrix porosity. Based on hand tests, geologists primarily describe fine-grained soils in terms of their toughness, plasticity, and dilatancy. With practice, these hand tests quickly and accurately distinguish between silts and clays, both predominant aquitard units at most LUFT sites. Therefore it is recommended that the USCS/ASTM system be used as a minimum. However, this system alone is insufficient for coarse-grained soils. Further description of coarse-grained soils is recommended in terms of texture, composition, and sedimentary structures in sufficient detail to interpret depositional environment (e.g., see Berg 1979).

All logged intervals should, at a minimum, begin with ASTM/USCS Group Symbols and Group Names, followed by Munsell Colors, text plus hue, value, and chroma codes. For fine-grained soils ( $\geq 50\%$  finer than #200 sieve), descriptions should continue with plasticity, toughness, and dilatancy. Descriptions should also include reaction with hydrochloric acid (HCl), soil (pedogenic) structures, cementation, root bores, and accessory minerals, as appropriate. For silts, Group Symbol ML (especially those with Group Names *Silt with Sand*), and *Sandy Silt*, also log appropriate *sedimentary* structures.

For coarse-grained soils or sediments ( $< 50\%$  finer than #200 sieve) descriptions should continue with texture, composition, and sedimentary structures. Texture should generally include total size range and modes, in millimeters (mm), grain shape, using the Powers (1953) chart for sands or USCS/ASTM for gravels, and estimated sorting. Efficient estimates of grain size distributions are feasible in the field; the LUFT Manual suggests conducting water-settling tests in a graduated cylinder. Textural descriptions should be sufficient to describe vertical grading within permeable units (e.g., fining- and coarsening-upward sequences).

Composition information should include hand-lens estimated percentages of quartz, feldspars, and rock fragments, normalized for sand and larger particles. Composition should also include accessory minerals (e.g., heavy minerals and muscovite) and fossils.

All descriptions should end with, or otherwise emphasize, field moisture content and evidence of pollution (e.g., staining, odor, sheen, PID reading). Additional discussion regarding soil boring descriptions can be found in Appendix B.

## Management of Investigation-Derived Waste

Drill cuttings and decontamination water are typical sources of investigation-derived waste (IDW) in soil investigations. The cuttings and water must be properly containerized and stored, sampled, and analyzed for COCs, and disposed of in accordance with regulatory requirements based on the concentration of COCs in the waste.

## Grouting of Soil Borings

Soil borings or DPT holes must be grouted in accordance with regulatory requirements. These requirements may vary with hole depth (e.g., above or below the water table), and different agencies allow for the use of different grouting materials (e.g., high-solids bentonite slurry, Portland cement, or cement-bentonite mixtures). Grout is typically placed into the hole from the bottom to the top using a tremie or pump to ensure that the borehole is completely filled and that bridging in the hole does not occur.

# Site Assessment



## Groundwater Investigation: Grab Groundwater Samples

Version 1.0 - Draft August 2010

Groundwater investigations at a LUFT site are conducted to determine whether the release from the UST has migrated and impacted the water-bearing zones beneath the site. Several methods are available to accomplish the collection of a “grab” or screening groundwater sample without bearing the expense of installing a groundwater monitoring well.

### Laboratory Analysis and Methods

The analytes and analytical methods for groundwater samples at LUFT sites are discussed in the [Laboratory Analysis and Methods](#) chapter of this Manual. In addition, the Analytical chapter provides information on testing for forensic purposes of free-product samples.

### Direct-Push Methods

“Grab groundwater” samples are routinely collected using direct-push rigs (for example, Geoprobe or CPT). These methods typically rely on the emplacement by DPT of a groundwater sampler with a shielded screen to a specified depth, retraction of the sampler to expose the screen, and collection of the sample by either retrieving the entire sampler or by lowering a miniature bailer or tubing into the sampler to retrieve the sample.

There have been many generations of DPT samplers since the early 1990s. The most commonly used are Geoprobe equipment and the Hydropunch. These grab groundwater samples are frequently used to identify the lateral and vertical extent of a groundwater plume prior to installing monitoring wells. Care needs to be exercised to ensure that the samples are representative and are not confounded by cross-contamination or other problems. A key consideration in the choice of sampler and method of emplacement is the potential for cross-contamination of the sample from impacted soils above the water table or at the capillary fringe, or from shallower water zones. Also critical is whether the sample is to be collected across the water table or beneath the water table.

**Tip:** It is recommended that the stratigraphy of the target zone be assessed using continuous core or CPT before the groundwater samplers are deployed.

The use of DPT groundwater samplers is discussed in Publication No. EPA 540/R-04/005, Office of Solid Waste and Emergency Response (OSWER) No. 9200.1-51 and ASTM D6001-05.

A recent development (as of 2010) is the availability of small-diameter “pre-packed” well screens that can be emplaced with a DPT rig (EPA 540/R-04/005). The pre-pack is a polyvinyl chloride (PVC) well screen surrounded by a sand filter pack held in place by a stainless-steel mesh. The sand pack allows for development of the temporary sampling point so that turbidity of the water sample is reduced.

### Open Borehole Methods

Some grab groundwater samples are collected by inserting PVC screen and riser casing into an open borehole drilled by HSA or advanced by DPT soil coring. The quality of samples collected from these temporary wells has historically been relatively low because of the occurrence of high turbidity. These temporary wells that used pre-packed well screens can now be developed to reduce the turbidity of the groundwater samples collected.

### Turbidity Issues

Grab groundwater samples collected from the smear zone at LUFT sites frequently contain petroleum-affected soil, sheen, or product globules. The smear zone is the vertical interval near the water table where both separate-phase petroleum and water are present in the soil pore spaces. It has been shown that such samples are not representative of dissolved-phase concentrations, because the non-dissolved petroleum is included in the analysis (Zemo 2009). Turbidity can be reduced by the use of pre-packed well screens and development of temporary sampling points.

**Important!** Every effort should be made in the field to produce samples that are as low in turbidity as possible.

# Site Assessment



## Groundwater Investigation: Well Construction and Development

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Groundwater wells are installed at LUFT sites after it has been determined that groundwater has been impacted and the general location of contamination has been established based on the information gained from groundwater screening samples. The installation of wells allows for higher quality samples and permits multiple sampling rounds.

This section discusses the design and installation of two types of wells that are commonly installed at LUFT sites: groundwater monitoring wells and groundwater extraction wells.

**Legal.** Prior to installing a well, the responsible professional must ensure that the design and installation are in accordance with state and local regulatory requirements. The State of California requirements for monitoring wells are found in Department of Water Resources (DWR) Bulletin 74-90; each county may also have its own well standards.

### Monitoring Well Design and Construction

The design of a groundwater monitoring well includes the selection of the proper target zone and the proper selection of screen size and filter pack, as discussed in subsequent sections. Monitoring wells must be designed by or under the direct supervision of a licensed professional (geologist or engineer) with current California registration and experience in hydrogeologic investigations and monitoring well design and installation.

#### Selection of Target Zone

At petroleum release sites, monitoring wells have typically been screened across “the water table” irrespective of stratigraphy. This has evolved due to the historical regulatory requirements that sheen or product at the capillary fringe be observable in the monitoring well throughout the hydraulic year. This has resulted in many sites where the shallowest monitoring wells are screened primarily across fine-grained soils, and the bottom of the screen interval sometimes crosses coarse-grained soils. These conditions can result in samples with anomalous water-level measurements and chemical concentrations.

Site stratigraphy should be understood prior to selecting target zones for monitoring well screens. This is best achieved by collecting continuous-core samples via several exploratory borings prior to installing wells. Although wells screened across “the water table” may be desirable in the source area to evaluate the presence of mobile product, most of the dissolved-phase mass will migrate away from the source area through soil units with higher relative hydraulic conductivity—interconnected pore spaces that allow water to flow through—typically coarse-grained sediments such as sand or gravel. For sites with heterogeneous stratigraphy, therefore, these coarse-grained units should be selected as target zones for monitoring wells outside the source area.

If a well is being installed to monitor a “deeper” zone (which is presumably less impacted than the “shallow” zone), it is important to seal off the shallow zone during drilling and well installation to avoid or minimize cross-contamination or drag-down. This is particularly important in the LNAPL source area.

#### Selection of Screen Size and Filter Pack

The proper selection of screen size and filter pack for the target zone allows for adequate well efficiency and the production of low-turbidity samples. Well-intake design is based on the lithology of the target zone and the purpose of the well. The common “generic” construction of Lone Star #3 filter sand and 0.020-inch slot screen frequently results in turbid samples, because the #3 sand is too coarse for the target zone. The selection of well-screen slot size and filter pack can involve a “rigorous” procedure or an “intermediate” procedure, depending on project requirements. The rigorous approach is based on sieve analysis of soils from the target zone, which can be performed in the field. Results from the sieve analysis are employed in the classic design method presented in *Groundwater and Wells* (Driscoll 1986). The filter pack retains 70% of



the target formation, and the screen retains 90% of the filter pack. This procedure and its advantages for environmental monitoring wells are documented in Reynolds and Zemo (1992 [ASTM STP 1118]).

An intermediate approach to selection of screen size and filter pack for groundwater monitoring wells is based on field experience, and does not require sieve analysis. Rather, this approach relies on visual estimates of grain-size distribution in the target zone and uses off-the-shelf filter packs and screen slot sizes. Based on field experience, a target zone that contains more than 30% fines (e.g., silty sand or finer) calls for a Lone Star #0/30 sand filter pack (or grain-size equivalent) and a 0.010-inch slot size screen. Target zones with 30% or fewer fines can be completed using a Lone Star #2/16 filter pack (or equivalent) and a 0.020-inch slot size screen. To maximize well efficiency, medium sand or coarser target zones with 15% or fewer fines can be completed using Lone Star #3 or #2/12 filter pack (or equivalent) and 0.030-inch slot screen.

### Monitoring Well Installation

The borehole into which the well will be installed can be drilled using several methods as described above, “Soil Investigation Methods,” including HSA, rotary, and sonic. The key criteria for selection of drilling methods are related to the well construction: target zone depth, inside diameter of the well casing needed for passing of pumps and sampling tools, and a borehole diameter that is at least 4 inches larger than the outside diameter of the well casing.

In general, wells are typically constructed with threaded Schedule 40 PVC blank casing. In cases of deep wells, Schedule 80 PVC may be used because of its greater strength to withstand the increased pressure. The inside diameter of the casing must be large enough to pass probes and purge/pump/sampling equipment. The well screen will usually consist of threaded machine-slotted PVC or wire-wrapped screen. The slot size for the well screen will be compatible with the filter pack and the target zone (see discussion above). The bottom of the well screen will be fitted with a threaded end cap.

After placement of the casing and screen assembly into the borehole, the annular fill is emplaced.

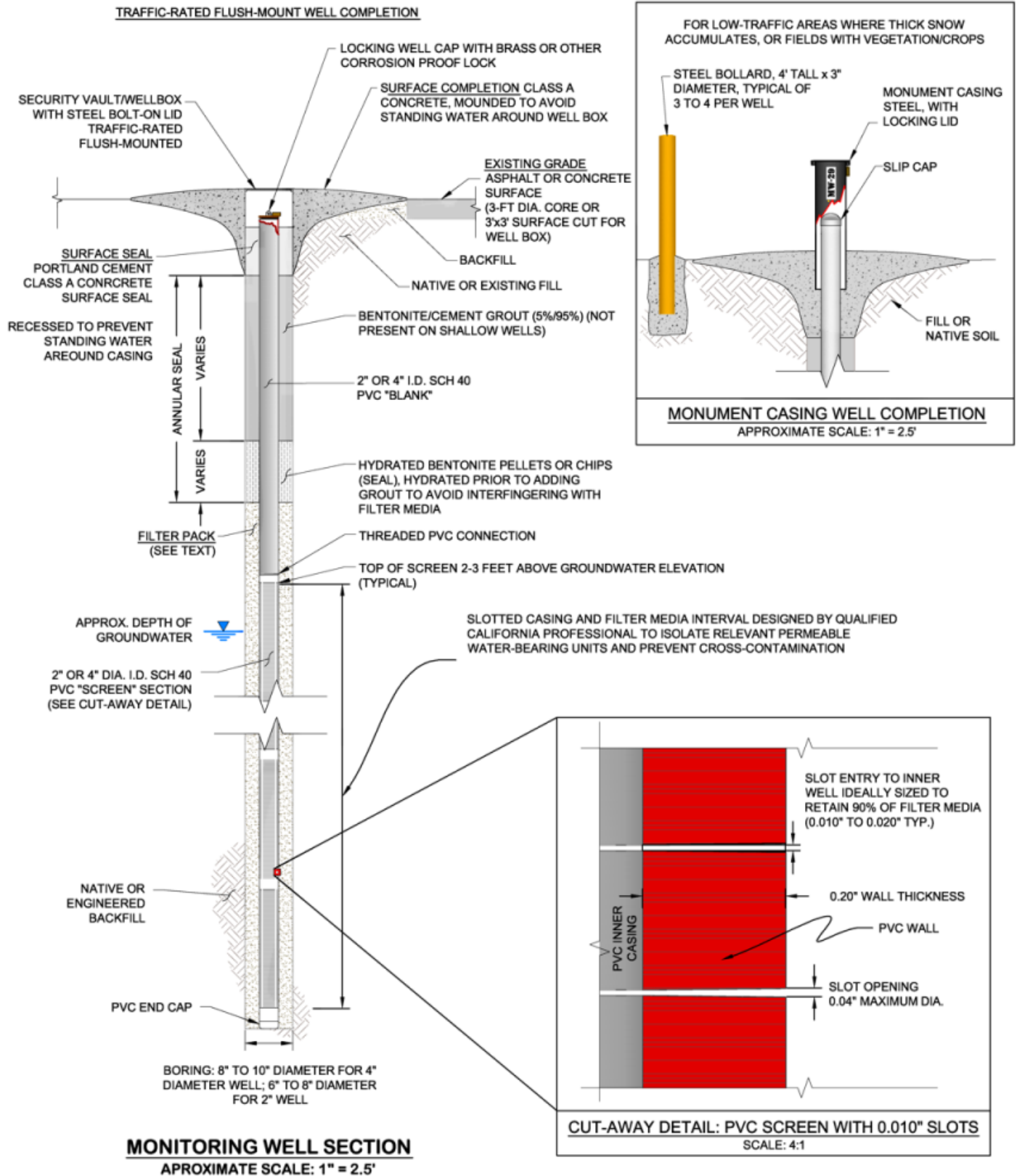
**Important!** Borehole stability during well installation is very important, to ensure that annular fill and seals are emplaced properly with no bridging or particle-size segregation.

The filter-pack sand will be poured or tremied into the annular space around the well screen. The filter sand is usually placed to a depth of 1 to 2 feet above the top of the well screen. A bentonite transition seal is then poured or tremied into the annular space above the filter sand. The transition seal is usually 1 to 2 feet thick, and must be fully hydrated. A neat cement grout, cement/sand grout, cement/bentonite grout, or high-solids bentonite grout is then placed from the top of the transition seal to the ground surface. The grout seal is usually pumped or tremied into the annular space. The seal thicknesses and grout/additive/water mixtures are determined on a site-specific basis, usually due to the depth of the well and local regulatory requirements. Depending on local regulatory requirements, an inspector may observe the placement of the grout seal. The grout must set for at least 48 hours before the well can be developed. See Figure 7 for an example of monitoring well construction.

**Important!** It is important that the required volumes of fill be calculated and compared to the real-time field amounts so that any bridging is detected and eliminated as the fill is being installed.



Figure 7 - Monitoring Well Construction Diagram



REFERENCE: DRISCOLL, F.G. (1986). "GROUNDWATER AND WELLS" JOHNSON FILTRATION SYSTEMS, INC. ST. PAUL, MN. PAGE 1021.

The surface completion for the well is determined on a site-specific basis. The objective for the surface completion design is to reduce the potential for entry of surface water runoff or foreign matter into the well and to secure the well from unauthorized entry. Surface completions can be at or below grade (e.g., traffic-rated vault or Christy box) or above-grade (e.g., steel protective stovepipe). Surface completions often have to make up grout volume at the top of the borehole due to grout shrinkage in the annular space. Well-completion forms must be filed with the DWR.

Wells installed for remediation purposes must be designed according to site-specific requirements and are discussed in the [Remediation](#) chapter of this Manual. The design of such wells must be approved by the permitting agency before the wells may be installed.

### Wells Designed to Monitor Multiple Zones

Often, it is desirable to monitor multiple water-bearing zones at one location to profile the vertical distribution of COCs or hydraulic head. The most common way to achieve this is to use a well cluster, where wells of different depths are installed in separate, but closely spaced, boreholes. A second way to achieve this is to install “nested” wells, where several wells of different depths are placed within one large borehole and the annular fill is emplaced in stages of filter pack and grout seal, according to the depths of the well screens. A third way to monitor multiple zones is where one “casing” is placed in one borehole, and the “casing” has multiple sampling ports at different depths. Examples of this type are the continuous multi-channel tubing system (CMT) and the Westbay system. In these cases, the annular fill is installed in stages of filter sand and grout seal, according to the depths of the sampling ports.

The use of nested wells or multi-port systems may be controversial and should be approved by the regulatory agency. The pros of these methods are that they can be less expensive for monitoring many target zones than installing separate wells. The cons are that the correct placement of the annular fill takes great care, the grout between the filter sand intervals may shrink and leave voids in the annular space, and the destruction of nested wells is usually more difficult because multiple casings are in one borehole.

### Groundwater Extraction Well Design

There are two typical objectives for groundwater extraction wells: hydraulic containment and removal of COCs from groundwater.

The two key issues in the design of groundwater extraction wells are:

- 1) The **inside diameter of the casing** necessary for installation of a pump of adequate size for the design flow rate, and
- 2) Careful design of the **screen interval** (filter pack and screen slot size) for maximum well efficiency and reasonably low turbidity.

It is recommended that the rigorous approach described in Driscoll (1986) be used to design an extraction well, especially for wells that are expected to have high flow rates. Also, because water-level measurements from within the pumping well are affected by well efficiency, it is common that a small-diameter piezometer be installed within the annulus to measure water levels in the filter pack. In soils with low hydraulic conductivity, the borehole can be over-drilled a few feet and a section of blank casing threaded to the bottom of the well screen to allow for a sump and dewatering of the target zone. The annulus against the blank casing beneath the screen should be filled with bentonite. Otherwise, the construction materials and installation methods are similar to those described for monitoring wells.

### Groundwater Well Development

Selection of the appropriate well development method depends on site-specific conditions and local regulatory requirements.

The purposes of well development are to:

- Remove sediment accumulated in the well during construction.
- Remove/mitigate borehole wall damage due to drilling.
- Allow water to flow more freely toward the well.
- Consolidate the filter pack around the well screen, remove the fines from the filter pack, and from the target zone adjacent to the filter pack.
- Provide hydraulic connection between target zone and well screen.

**Note.** Well development is NOT simply purging. It is an active procedure designed to accomplish the listed goals and to yield low-turbidity, high-quality samples from the well. Recent work has shown that turbid groundwater samples collected from monitoring wells in the smear zone produce unrepresentative data that are biased by the petroleum-affected turbidity (Zemo 2009).

Development of wells is usually accomplished by an iterative process that involves bailing fines from the well, surging the screen area with a surge block or other device, and over-pumping at a rate exceeding the anticipated purge rate for sampling. Fines should be bailed out of the well several times during development. Bailing of fines is necessary to remove them from the well and to protect pumps. This iterative process continues until the return water is observably clear. Field parameters such as temperature, specific conductance, and pH provide valuable information, but their stabilization does not indicate the completion of well development. Likewise, there is no set number of casing volumes removed that indicates the completion of well development. The bailing, surging, and pumping process continues until the produced water is visually clear.

Development of wells screened across fine-grained soils can be very time-consuming because of the low percent open area of the required slotted well screen and low transmissivity of the formation. Field staff need to spend the time required to complete the well development. If the target zone recharges too slowly, potable water can be added to the casing to assist with surging. The amount of added water must be documented so that the same volume, at a minimum, is pumped out of the well before development is completed.

Likewise, development of wells installed in mud-rotary boreholes can be time-consuming because the filter cake must be broken up and lost drilling mud recovered before development can progress.

**Important!** It is important to over-pump the well during development at a rate that exceeds the anticipated purge rate for well sampling or extraction.

If the well is later purged or pumped at a higher flow rate, fines can be mobilized into the well and the well will need to be re-developed.

There are various methods that can be used to “pump” the well during development, including submersible pumps and air-lifting. Pumping may be difficult to accomplish if the entrance velocity from the formation to the well is not high enough to move the fines, either in the formation or the filter pack. This is one reason many shallow monitoring wells do not develop sufficiently to yield non-turbid samples. The gravel pack usually has more than enough transmissivity to provide the well yield for a monitoring well. However, the open area for smaller well screen slots can generate higher entrance velocities, resulting in the movement of fines into the well. A developed well may generate fines later if the groundwater level rises in the well, resulting in higher entrance velocities than were possible when the well was initially developed.

**Important!** Water produced during well development typically needs to be contained, so it’s important to have adequate containment onsite before the development begins (e.g., tanks or drums). Water, sediment, and other waste removed from a well during development operations must be disposed of in accordance with applicable federal, state, and local requirements.

## Well Destruction

Wells can be destroyed by several methods, depending on site-specific conditions and regulatory requirements.

**Legal.** The State of California requirements for well destruction are found in DWR Bulletin 74-90.

Local agencies frequently have their own requirements for well destruction, so the responsible professional must ensure that well destruction is conducted in accordance with applicable regulatory requirements. For shallower wells, a typical method involves drilling out the casing and annular fill and pressure-grouting the resulting borehole from the bottom to the ground surface. For deeper wells or larger extraction wells, the casing can be cut from bottom to top and then the inside of the casing pressure grouted. Grouting materials must be approved by the regulatory agency, and an agency representative

is typically present during a destruction event. Well destructions are documented using forms from DWR and the local agency.

**Legal.** DWR Bulletin 74-90 requires that monitoring well construction, alteration, and destruction reports be completed on forms provided by the California Department of Water Resources.

## Well Survey

Well locations should be surveyed for horizontal and vertical control by a California Registered Civil Engineer or licensed professional surveyor. These coordinates are typically referenced to a United States Geological Survey (USGS) datum. The x, y, and z coordinates for each well at a site are also required to be uploaded to GeoTracker. The coordinates should also be reported in the site assessment report.

# Site Assessment



## Groundwater Investigation: Monitoring Well Sampling

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Groundwater monitoring well sampling (groundwater sampling) is a critical component of LUFT site management, because trends in concentrations, natural attenuation or the response to remediation can be monitored. Effective groundwater monitoring requires consistent methods of gauging, sampling, and sample handling and analysis. Information obtained during groundwater monitoring includes depth to groundwater, thickness of separate-phase hydrocarbons (SPH) ("free product") if present, concentrations of COCs, and measurements of general chemistry parameters.

**Note.** Historic groundwater level evaluation may dictate the collection of deeper groundwater samples consistent with recorded historic water levels near the dates of potential site releases.

### Laboratory Analysis and Methods

The laboratory analysis and methods for groundwater samples at LUFT sites are discussed in the [Laboratory Analysis and Methods](#) chapter of this Manual. In addition, the Analytical chapter provides guidance regarding testing for forensic purposes for free product samples.

**Important!** To be useful, data collected during different monitoring episodes, even by different consultants or over a long period of time, must be comparable.

### Gauging

Gauging a well is completed prior to sampling to determine the depth to the bottom of the casing, the depth to the water surface, and the thickness of free product (if present). Gauging is done using electronic devices or a graduated tape treated with water- or hydrocarbon-sensitive paste. Prior to taking a measurement, adequate time should be allowed for the open well to equilibrate with atmospheric pressure. Depths are recorded to the nearest 0.01 foot relative to a surveyed reference point. If NAPL is present, the measured depth to water is to be corrected using the following formula:

$$DTW_c = DTW_m - (TSPH \times SGSPH)$$

where:

- DTW<sub>c</sub> = Corrected Depth to Water
- DTW<sub>m</sub> = Measured Depth to Water
- TSPH = Thickness of Separate-Phase Hydrocarbons
- SGSPH = Specific Gravity of Separate-Phase Hydrocarbons

The specific gravities for some fuels are:

- Gasoline: 0.75 gram per cubic centimeter (g/cm<sup>3</sup>)
- Diesel: 0.81 g/cm<sup>3</sup>
- Jet Fuel (JP-4): 0.79 g/cm<sup>3</sup>
- Fuel Oil #2: 0.91 g/cm<sup>3</sup>
- Fuel Oil #6: 0.96 g/cm<sup>3</sup>



**Note.** If blank casing was installed below the screened interval when a well was constructed, that well is not monitored unless the water level is at least 2 feet above the base of the screened interval. Otherwise, the gauged depth to water may be incorrect, and any samples collected will include the stagnant water inside the blank casing, or water which cascaded into the blank casing after it was purged.

Potential causes of anomalous water level measurements include:

- Leaking sewer lines
- Well screened improperly
- Inaccurate survey data
- Vertical flow
- Hydraulic continuity with underground utilities

## Groundwater Sampling Procedures

As with soil sampling, there are many groundwater sampling guidance documents available. “Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring” (Nielsen 2006) and “Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers” (EPA 2002a) are two comprehensive references.

If free product or sheen is present in a well, it should not be purged and sampled under most circumstances because the water sample is not representative of the dissolved phase. However, in the case where a product sample is desired or special laboratory handling will be used to isolate the water phase (see the [Laboratory Analysis and Methods](#) chapter), a sample may be collected.

Water samples are collected using equipment which minimizes the chance of volatile constituents escaping from the sample. Dedicated submersible pumps, bladder pumps, peristaltic pumps, and bailers (preferably single-use) are acceptable. Air-lift pumps may not be used. If reusable bailers are used, the bailer must be thoroughly decontaminated and a new cord attached before each sample is collected.

To minimize the possibility of cross-contamination, sampling proceeds from the least contaminated to the most contaminated wells, and non-dedicated sampling equipment is completely decontaminated between sampling events. Decontamination requires thorough washing of the sampling equipment with an appropriate cleaning solution, rinsing it twice with clean tap water, and rinsing it a third time with deionized or distilled water.

Samples are transferred from the sampling equipment to the appropriate collection containers carefully, to minimize mixing with ambient air. For samples that will be analyzed for volatile or semi-volatile compounds, the container is filled completely so that no headspace is present. Fill the sample container so there is a meniscus, (the sample liquid rises above the lip of the sample container). Then carefully place the cap on the container and screw it down tightly. The presence of headspace can be checked for by inverting the sealed container, tapping it lightly, and looking for bubbles. If bubbles are present, another sample is needed to ensure accurate data. However, if the water or the sediment in the water contains calcium carbonate, bubbles will be generated, even in the absence of headspace. In this latter case, the usual hydrochloric acid (HCl) preservative is not added to the sample containers on subsequent samplings.

**Note.** Not using acid as a sample preservative affects the laboratory holding times and should be considered to avoid exceeding holding times.

Samples are collected in containers and in the quantities appropriate for the requested analyses. All samples are labeled, properly sealed, and preserved according to stated laboratory requirements. Proper chain-of-custody procedures need to be followed, including: no time gaps between field sampler(s), courier, laboratory, or other handler(s) of the samples. The appropriate holding times for the sample medium, analytical method, and preservative used must be strictly observed.

**Note.** Check with your laboratory regarding any specific sample collection, volume, or handling procedures they might require, which may be different from standard protocols.

## Purging

The overall objective of groundwater sampling is to collect samples that are representative of *in-situ* groundwater conditions. Sampling of groundwater monitoring wells has traditionally involved purging to remove stagnant water in the well casing. Purging involves the removal of sufficient water from a well to ensure that the samples are representative of the groundwater in the impacted zone rather than simply standing water from within the well. Purging is generally conducted using the method employed for sampling.

Three methods are discussed below. RPs should consult with their regulator regarding acceptable methods.

### Conventional Method of Purging

Three or more casing volumes of water is the traditional volume required for purging a monitoring well with a bailer or pump to remove stagnant water above the screened interval prior to collecting samples. Water-quality indicators, including pH, temperature, visual turbidity, and specific conductivity of the extracted water are monitored throughout the purging process. Purging continues until conditions are stable (i.e., the variance between sequential conductivity measurements is 10% or less). The purged volumes at which measurements are collected, the measured values, the total volume of water removed, any anomalies noted (odor, color, high sediment content, etc.), and the time purging began and ended are reported for each well. It is important that a consistent purging protocol be followed during each sampling event. Changes in sample pumps (flow), depths where purge pumps are placed, volumes removed, etc., can alter the sample results gathered during that particular sampling event.

- Boring volume in gallons can be calculated using the industry standard rule of thumb:
  - 2-inch well: 3 volumes =  $\frac{1}{2}$  of the water column height (in gallons)
  - 4-inch well: 3 volumes = 2 times the water column height (in gallons)
- After purging, a well is generally allowed to recover to at least 80% of the static water level before samples are collected.
- Care should be taken not to purge slow-recharge wells dry. If that does happen, water may cascade into the well from unknown intervals, and the samples obtained may not be representative of groundwater conditions. Therefore, the rate of purging and/or the volume of water removed from wells that are historically slow to recharge are adjusted accordingly.

### Low-Flow Purging

Low-flow purging (or micropurging) does not require the removal of large volumes of water. In micropurging, groundwater is pumped at a low flow rate (less than 1 liter per minute or 0.25 gallons per minute) from within the well screen. This technique minimizes the mixing of overlying stagnant casing water and water within the screened interval. In addition, sample turbidity is reduced. Water-quality indicators, including pH, temperature, dissolved oxygen (DO) oxidation/reduction potential (ORP), turbidity, and specific conductivity of the extracted water are monitored throughout the purging process within a flow-through cell (e.g., YSI® Sonde). Purging continues until conditions are stable (i.e., the variance between sequential conductivity measurements is 10% or less). The purged volumes at which measurements are collected, the measured values, the total volume of water removed, any anomalies noted (odor, color, high sediment content, etc.), and the time purging began and ended are reported for each well. It is important that a consistent purging protocol be followed during each sampling event. Changes in sample pumps (flow), depths where purge pumps are placed, volumes removed, etc., can alter the sample results gathered during that particular sampling event (Puls and Barcelona 1996; Kaminski 2003).

This low-flow technique has several advantages over traditional purging:

- Less turbid samples are produced.
- Less volatilization occurs.
- Sampling accuracy and precision are improved.
- Low pumping rates preserve the integrity of the filter pack and well seal and reduce the movement of fine sediments into the well.
- Lower volumes of purge water requiring storage, treatment, or disposal are generated.

## No-Purge Sampling

No-purge sampling is conducted by carefully lowering a bailer to the water table and allowing it to fill with minimal disturbance of the water column, without prior purging of the well (American Petroleum Institute [API] 2000).

The method is applicable at sites with unconsolidated, unconfined water-bearing units and only at wells screened across the water table. No-purge sampling should not be used at wells where free product is present. It *should* be considered for sites where high-precision sampling is not needed, e.g., for routine monitoring. It *should* be supplemented with conventional or low-flow techniques. This method is quick and inexpensive and may eliminate the variability introduced by purging. In addition, purge-water management and disposal costs are eliminated.

### Passive Samplers

A type of no-purge groundwater sampling can be performed with passive samplers. These passive samplers remain submerged in the monitoring well for a specified time period. The passive sampler type must be matched to the chemicals being monitored (The Interstate Technology & Regulatory Council [ITRC] 2007a, ITRC 2004, ITRC 2002).

## Decontamination

The following procedures may be used for decontaminating both soil and groundwater sampling equipment:

- **Drilling and/or Other Equipment:** Drill bits, augers, and other equipment coming into contact with sampling media should be steam cleaned between borings and after each use.
- **Sampling Equipment:** Sampling utensils are either a) properly decontaminated between each use, or b) dedicated to each location and disposed of after use.
  - *Reusable bailers* are steam cleaned; otherwise, one-time-use, disposable bailers are used.
  - The *cord* used with reusable bailers is discarded after each use.
  - *Sampling equipment that is not steam cleaned* is initially washed with a non-phosphate detergent, rinsed twice with tap water, and final-rinsed with deionized or distilled water. Depending on the site-specific COCs, an additional acid, base, or solvent rinse may be included.
- **Rinsate Blanks** (Equipment Blank) are obtained by passing distilled or deionized water, as appropriate, over or through the decontaminated equipment used for sampling. They provide the best overall means of assessing contamination arising from the equipment, ambient conditions, sample containers, transit, and the laboratory (USEPA 2000). The soil and water from washing, rinsing, and steam cleaning are sampled, properly containerized, and labeled for disposal.

## Waste Disposal

Soil, groundwater, and other IDW should be properly containerized, labeled, and analyzed for appropriate disposal.



# Site Assessment

## Soil-Vapor Investigation



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### Soil-Vapor Survey

Vapors released by the presence of COCs in soil and groundwater can often be identified by analyzing trace gases just below the ground surface. Soil-vapor surveying is a preliminary investigation technique used to confirm the presence of vapors in the subsurface environment, and can serve to direct further soil and groundwater investigations.

Soil-vapor sampling measures the concentration or flux of volatile compounds in soil pore spaces. Sampling techniques may be either *passive* or *active*. Passive methods use a sorbent sampling device that is buried for a specified time interval, and then retrieved for sample extraction and analysis. Active methods consist of withdrawing samples of soil vapor through a probe driven into the vadose zone. These samples are commonly analyzed by an on-site mobile laboratory. Soil-vapor surveys can provide relatively rapid and cost-effective site data.

**Further Reading.** Please see ITRC guidance for preferred methodology, available on the Internet at: <http://www.itrcweb.org/Documents/VI-1.pdf>

The soil-vapor survey described in this section is distinguished from a vapor intrusion (VI) investigation. If the presence of vapors is identified, a more extensive VI investigation may be warranted. Additional information regarding sampling techniques for a VI investigation is described in detail in Appendix C.

### Laboratory Analysis

The analytical methods selected for a soil vapor investigation are dependent upon the regulatory requirements and data quality objectives (DQOs) for a given site. Fixed labs, mobile labs, or field monitoring equipment may be suitable for the purpose, provided that the method detection limits and quality assurance/quality control (QA/QC) are appropriate for the intended use of the analytical results.

The target analytes and analytical methods for vapor samples are discussed in the [Laboratory Analysis and Methods](#) chapter.

### Soil-Vapor Sampling

Methods for shallow soil-vapor sampling are described in numerous documents (DTSC 2005; USEPA 2002b; ITRC 2007b; API 2005).

Soil-vapor samples are usually collected by one of the three following methods. Care must be exercised during sample collection to ensure that the quality of the samples is appropriate for the intended use. The loss of volatiles during sampling is a constant concern.

- **Active Soil-Gas Sampling:** Vapors are actively withdrawn from the ground. This method produces quantitative values. The active method is the most frequently used method in vapor investigations.
- **Passive Soil Gas Sampling (limited use):** An absorbent is buried in the ground and vapors are allowed to contact the absorbent. The absorbent is collected for measurements. This method does not provide quantitative data and therefore cannot be used for risk applications; however, it can be used for screening.
- **Flux Chambers (limited use):** Flux Chambers are used to determine levels of VOCs emitted from land or liquid surfaces. The Flux Chamber is set up to enclose a known surface area. Air is introduced to the chamber to mix with the emissions and transport them to the collection devices. The Chamber is designed to create the best mixing and sampling conditions without altering the emission of gases at the surface. The samples collected are used to determine the actual flux of VOCs at the surface.

## Active Soil-Gas Sampling

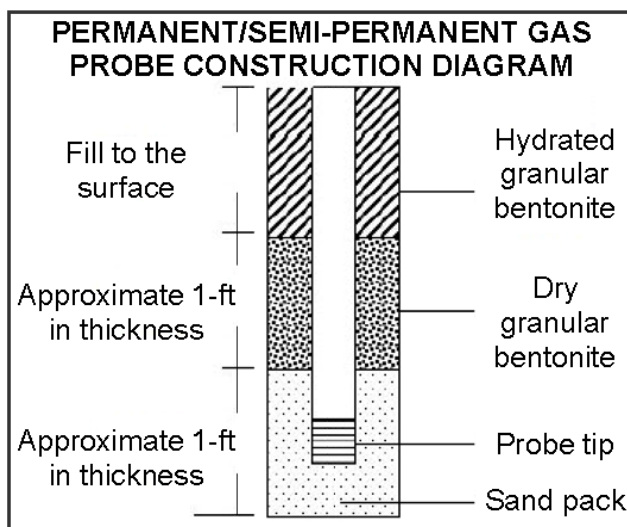
Active soil-gas sampling is commonly performed by installing a temporary or semi-permanent probe in a borehole. Several methods are used to collect soil-vapor samples (Los Angeles Regional Water Quality Control Board [LARWQCB]/DTSC 2003; ITRC 2007b).

### Permanent or Semi-Permanent Soil-Gas Probe Methods

Permanent or semi-permanent soil gas probes may be installed using a variety of drilling methods. The mud rotary drilling method is not acceptable for soil-gas probe emplacement. Other drilling methods, such as air rotary and roto sonic, may adversely affect soil-gas data during and after drilling and will require extensive equilibration times; therefore, they are not recommended. Other soil-gas probe designs and construction (e.g., soil-gas wells or nested wells) may be appropriate and should be discussed with regulatory staff prior to emplacement (LARWQCB/DTSC 2003). LARWQCB/DTSC offers further details on probe installation in *Advisory – Active Soil Gas Investigations*, January 28, 2003. See Figure 8 as an example of the construction of a soil gas probe.

**Tip:** Soil-vapor samples collected through direct-push rods in low-permeability soils may have problems with leakage of ambient air around the drill rod. Leak tests should be conducted during sample collection to document that the sample is representative of soil-vapor conditions.

Figure 8 – Soil Gas Probe Construction Diagram



### Temporary Soil Gas Probe Emplacement Method

In general, the drive rod is driven to a pre-determined depth and then pulled back to expose the inlets of the soil gas probe (LARWQCB/DTSC 2003). LARWQCB/DTSC offers further details on probe installation in *Advisory – Active Soil Gas Investigations*, January 28, 2003.

# Site Assessment

## Lessons Learned

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### Introduction

**Notice to the Public:** This chapter contains many ideas for “lessons learned.” Some of these items have been discussed; however, many still require input. Please submit input or comments at to [luftmanual@onesullivan.com](mailto:luftmanual@onesullivan.com).

### Anomalous Water-Level Data

#### Spaghetti Contours – What do these tell us?

We will consider “spaghetti contours” to be a site plan showing groundwater elevations which do not make sense. These contours will include water-level elevations in nearby wells which are not consistent and from which there cannot be calculated any obvious flow direction or gradient.

There are numerous reasons why this might occur at a site, and these can be categorized into two basic categories: operator error and hydrogeologic site conditions.

#### *Examples of Operator Error:*

- Attempting to contour water-level elevations using data obtained from multiple aquifers (perched, water table, confined, or from aquifers with larger vertical upward or downward gradients).
- Collecting water-level data before wells have had time to equilibrate after opening well cap.
- Failing to measure depths to water with sufficient speed in areas with significant tidal influences.
- Using measurements from wells which have filled with sediment or from wells which have become plugged in some manner. Sediment can block off a water-bearing zone and alter the water-level measurements (this effect can be gradual or show up immediately).

#### *Examples of Hydrogeologic Site Conditions Causing Error:*

- Rapid changes in stratigraphy across a site, such as a stream channel meandering with coarse material adjacent to and interlaced with fine-grained material.
- Pods of low-permeability material can create a semi-confined condition in an otherwise water-table (unconfined) aquifer. The results can be water-level elevations that don’t track evenly across a site.
- Wells located next to buried utilities where well perforations have hydraulic continuity with the utility backfill.
- Wells located near to and in continuity with a former or current UST pit (can result in anomalous high or low water levels).
- Perched water zone on a portion of a site.
- Wells perforated across two or more water-bearing zones with different hydraulic heads.
- Well measurements taken immediately after a major rainfall event and before the aquifer system has time to equilibrate.
- Some of these issues can be easily resolved by graphing the water elevations each monitoring period and comparing the new elevations with the historical water-level monitoring data. It will be very apparent which well elevations track consistently with each other and which wells do not. When a well does not track consistently, seek out a reason.

#### Consistent Data Points

If the depth-to-water-level measurements in a monitoring well or wells is always the same, or varies very little, when other wells at a site show variance, this could signal that water levels have fallen below the screened interval of the monitoring well and that only residual water in the well’s end cap is being measured. In this case, water-level measurements should be compared with the known total depth of the well, or the very bottom depth of the well should be measured and compared to the water-level results.

## Anomalous Gradients

If data from one or more adjacent or nearby sites to the site being monitored differ significantly from what the data show for the site in question, it is possible that well casings have been cut, that they sank due to high traffic in the area, or that they were not accurately surveyed for top-of-casing elevation. It is appropriate to attempt to determine if this is the case when trying to explain anomalous water levels or flow directions at a site.

## Issues with Computer-Generated Groundwater Contour Maps

Many computer-generated contour maps do not allow for professional geologic interpretation of a site's specific features, which should be taken into account prior to drawing groundwater contours.

## Sampling Sheen or Non-Dissolved Petroleum

Collecting groundwater samples within the smear zone often results in the inadvertent collection of sheen or non-dissolved product in the sample due to (even minor) turbidity caused by the very act of sampling itself. This occurs both in wells and in grab-groundwater samples. Inclusion of a non-dissolved component has been documented to cause reported concentrations of analytes in groundwater to be biased high. Every effort should be made to avoid sampling sheen and to reduce sample turbidity in the field so that analytical results are more representative of the dissolved-phase concentrations in groundwater.

## Semi-Confined Aquifers

The two ends of the spectrum of types of aquifers are *confined* and *unconfined* (with *semi-confined* in between). Semi-confined aquifers are partially confined by soil layers of low permeability, through which recharge and discharge can still occur. Unconfined aquifers are sometimes also called water-table or *phreatic* aquifers, because their upper boundary is the water table (*phreatic* surface). The shallowest aquifer at a given location is typically (but not always) unconfined, meaning it does not have a confining layer (an aquitard or aquiclude) between the aquifer and the surface. Unconfined aquifers usually receive recharge water directly from the surface from precipitation or from a body of surface water (e.g., a river, stream, or lake) with which it is hydraulically linked. The water table is located above the upper boundary of confined aquifers, which are typically located below unconfined aquifers.

If the distinction between confined and unconfined is not clear geologically (in the case where it is not known whether a clear confining layer exists, or if the geology is more complex, i.e., fractured bedrock), the value of storativity returned from an aquifer test can be used to determine whether an aquifer is confined or unconfined (although aquifer tests in unconfined aquifers should be interpreted differently from those in confined aquifers).

Confined aquifers have very low storativity values (much less than 0.01, and as little as  $10^{-5}$ ), which means that the aquifer is storing water using the mechanisms of aquifer matrix expansion and the compressibility of water, which are typically both very small quantities. Unconfined aquifers have storativities (typically called "specific yield" for unconfined aquifers) greater than 0.01 (1% of bulk volume). Unconfined aquifers release water from storage by draining the pores of the aquifer, which can release relatively large amounts of water (up to the drainable porosity of the aquifer material).

**Important!** When installing monitoring wells in a water-bearing zone that is either confined or semi-confined, it is important to take into account that, very often, the initially measured water level in the boring will rise up to much shallower levels. If proper monitoring well design and construction techniques are not employed during monitoring well installation, the data collected from the well may not be reliable.

## Historic Release Now Trapped Below Current Water Levels

An investigator cannot necessarily assume that the LNAPL smear zone will occur only at or near the current groundwater table. Fluctuating groundwater levels may create a zone of entrapped LNAPL well below, and disassociated from, the current water table. This can happen when released LNAPL migrates to the groundwater table during a period of lower groundwater levels followed by a period of rising groundwater levels. As groundwater levels rise, this LNAPL may become entrapped far beneath the groundwater table.

In order to initially assess the potential for the occurrence of LNAPL below the current water table, the investigator should try to understand the relationship between the timing of the petroleum releases at the site and historic groundwater levels beneath the site. If evidence suggests that petroleum has been released at the site during periods when groundwater levels

were significantly lower than current levels, which could occur during periods of drought or low precipitation, then the potential occurrence of LNAPL below the current groundwater table should be considered during the site assessment.

Common indications of entrapped or submerged LNAPL during site-assessment activities are:

- The occurrence of very high concentrations of dissolved petroleum hydrocarbons in groundwater (i.e., near solubility concentrations) without free phase product or sheen being observed on top of the groundwater.
- Concentrations of dissolved constituents that are significantly higher in “deeper” site wells as compared to “shallow” site wells.
- The absence of a smear zone at the water table during drilling but the appearance of LNAPL in monitoring wells after their installation.
- The absence of a smear zone at the current water table but the presence of LNAPL in soils well below the water table during soil sampling.

The presence of high TPH concentrations or LNAPL in soil samples well below the current water table with no evidence of LNAPL in shallower samples in a particular boring suggests that lateral migration of the LNAPL took place at a time when the water table was at the depth where the sample was collected. This can be useful in providing an indication of when the release occurred (at a time when the water table was deeper).

**Important!** The assessment of submerged LNAPL is important to properly evaluate the site and develop an efficient plan for site remediation. If its effective solubility is high enough, submerged LNAPL is potentially a significant source of dissolved constituents to the groundwater, and can lead to inefficient site remediation efforts if not detected and evaluated.

## Changes in Groundwater Flow Direction

The evaluation of groundwater flow direction is an important component of site assessment, especially if groundwater has been impacted. Groundwater flow direction is often fairly consistent beneath a site, with minor fluctuations observed due to seasonal changes. In some cases, however, significant changes in groundwater flow direction are observed, and can be attributed to a number of variables, including:

- Tidal effects.
- Groundwater levels beneath a site located near the ocean coastlines and bays or near tidal channels are often significantly affected by the ocean tides. Tidal studies where groundwater levels in monitoring wells are continuously monitored over a period of time (often during spring or neap tides) can be conducted to evaluate tidal effects. Collecting water-level measurements over a period of time covering a full tidal cycle can usually provide confirmation of whether the tidal effect is present at a site and what the approximate lag time is between the nearest tidal waters and the site.
- Seasonal gaining/losing streams.
- Groundwater levels can be significantly affected by seasonal recharge of groundwater from streams and channels during wet periods or by seasonal discharge of groundwater into streams and channels during dry periods. Sites near surface water bodies should be evaluated for potential gain and/or loss conditions.
- Human-caused changes in groundwater flow directions.
- Pumping of groundwater in nearby wells, including cyclic pumping or seasonal pumping, can significantly affect groundwater flow direction.

**Note.** Water levels at many sites track the water levels of nearby surface waters, including lakes, rivers and streams. Most of these water bodies have historical water-elevation data that can be used to evaluate historic trends. This is a different phenomenon from that of gaining/losing streams, and is different from normal seasonal groundwater fluctuations.

- Leaking pipes and water mains can create groundwater mounding beneath a site. The mounding can produce changes in groundwater flow direction or the occurrence of a radial groundwater flow direction.

- Inaccurate groundwater level measurements and, in some cases, damage to well casings at the surface (e.g., change in reference elevations) can produce erroneous changes in groundwater flow direction. If sudden changes of groundwater flow direction are observed, review of groundwater level measurements and well conditions on field sheets is generally recommended as an initial evaluation.

## When to Redevelop a Monitoring Well

Redevelopment is generally appropriate under the following conditions:

- Sediment accumulation in well.
- Well produces less, slower recharge.
- Groundwater contours have become erratic without known cause.

## Anomalous Detections of “TPHd” or “DRO”

“TPH” as measured using modified EPA Method 8015 is not sensitive to the actual constituents present in the sample, and therefore organic compounds other than petroleum can be quantified and reported by the laboratory in both the Gasoline Range Organics (GRO) and Diesel Range Organics (DRO) ranges. VOCs such as chlorinated solvents can be reported as “TPHg/GRO.” Laboratory contamination can be reported in either the “TPHg/GRO” or “TPHd/DRO” ranges. Natural organics and biodegradation byproducts can be reported in the “TPHd/DRO” range. Semi-volatile organics such as coal tar or creosote can be reported as “TPHd/DRO.” These detections are often flagged by the laboratory as “does not match standard,” but the concentrations are reported anyway.

**Important!** It is important to review the chromatograms to evaluate the source of the anomalous detections, and not to assume that the reported detections are petroleum.

## Importance of Good Record-Keeping and Field Notes

Another common pitfall is relying on differing interpretations by multiple geologists/loggers when creating cross-sections or making geological interpretations of a site.

To avoid this pitfall, review existing logs prior to drilling new borings. Ensure that the current geologist/logger is aware of previous observations and is familiar with standard procedures, including the USCS.

## Creation of Vertical Conduits by Improper Drilling and Well Installation/Destruction Methods

Drilling, well installation, and well destruction are important common components of site-assessment activities. If performed incorrectly, these activities have the potential to create vertical conduits which can allow contaminants to migrate vertically, increasing impacts to soil and/or groundwater.

Some examples of the formation of vertical conduits are:

- **Unsealed Boreholes:** Investigative boreholes that are left open can allow LNAPL to move into the boring and then downward through the open borehole annulus. This is especially likely to occur if the borehole is located in or near source areas. After completion, boreholes should be sealed as soon as possible using proper materials and methodology.
- **Improper Annular Well Seals:** Well seals that are improperly designed or improperly installed provide inadequate protection from groundwater. Annular well seals should be designed in accordance with California Monitoring Well Standards (Bulletin 74-90). Well seal design should take into account various subsurface factors including lithological changes (clay zones), location of aquifers and/or groundwater-bearing zones, and location of source areas, including impacted soil materials and LNAPL. Use of improper seal materials and improper installation techniques can lead to shrinking or cracking of the seal and bridging of materials, both of which can create open areas adjacent to well casings.
- **Improper Screen Locations/Intervals:** Improper screen locations, including installing long screened segments across impacted zones (both saturated and unsaturated) and screens that extend across different aquifers or zones of groundwater, can enhance the vertical migration of contaminants.

- **Lack of continuously cored borings at a site:** To avoid this pitfall, ensure that any lateral or vertical changes in geology are recorded on the boring logs of any boreholes advanced at the site.
- **Improper Destruction of Wells:** Improperly destroyed wells can leave open vertical conduits in the subsurface. Wells should be destroyed in accordance with California Well Standards (Bulletins 74-81 and 74-90).



# Site Assessment

## References



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- Aller, L., T.W. Bennett, G. Hackett, R.J. Petty, J.H. Lehr, H. Sedoris, D.M. Nielsen, and J.E. Denne. 1989. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. EPA/EMSL-Las Vegas, USEPA Cooperative Agreement CR-812350-01, EPA/600/4-89/034, NTIS #PB90-159807.
- American Society of Testing and Materials (ASTM). 1990. D2488-90. Standard Practice for Description and Identification of Soils.
- ASTM. 2004. Standard practice for design and installation of ground water monitoring wells in aquifers. D 5092-04.
- ASTM. 2005a. D 6001-05. Standard Guide for Direct-Push Water Sampling for Geoenvironmental Investigations.
- ASTM. 2005b. Standard guide for decommissioning of ground water wells, vadose-zone monitoring devices, boreholes, and other devices for environmental activities. D 5299-99-05.
- [ASTM. 2008. ASTM E2600 – 08 Standard Practice for Assessment of Vapor Intrusion into Structures on Property Involved in Real Estate Transactions.](#)
- American Petroleum Institute (API). 2000. No-Purge Groundwater Sampling, An Approach for Long-Term Monitoring, Newell, C.J., R.S. Lee, and A.H. Spexet, Groundwater Services, Inc. October.
- API. 2005. Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites. API Publication Number 4741. November.
- Barrow, J. 1996. US Patent 5549170 - Sonic drilling method and apparatus. US Patent issued on August 27, 1996.
- Berg, R.R. 1979. *Exploration for Sandstone Stratigraphic Traps*, American Association of Petroleum Geologists, Continuing Education Program, Course Notes Series #3. (Order through AAPG Continuing Education Program.)
- Blatt, H., G. Middleton, and R. Murray. 1980. *Origin of Sedimentary Rocks*, Second Edition, Prentice Hall, Englewood Cliffs, NJ, ISBN 0-13-642710-3.
- Chapelle, F.H., J.E. Landmeyer, and P.M. Bradley. 2000. "Identifying the Distribution of Terminal Electron Accepting Processes (TEAPS) in Ground-Water Systems" in EPA Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Summary, Dallas, TX, April 25-27.
- Driscoll, F.G. 1986. Ground Water and Wells, 2nd Edition. Johnson Division, St. Paul, Minnesota, 1089 pp.
- Department of Toxic Substances Control (DTSC). 1994. Application of Surface Geophysics at Hazardous Substance Release Sites, Guidance Manual for Groundwater Investigations. State of California – EPA. Department of Toxic Substances Control. August 1994 Interim Final.
- DTSC. 1995. Monitoring Well Design and Construction for Hydrogeologic Characterization: Guidance Manual for Ground Water Investigations. July. Available at: [http://www.dtsc.ca.gov/SiteCleanup/upload/SMP\\_Monitoring\\_Well\\_Design.pdf](http://www.dtsc.ca.gov/SiteCleanup/upload/SMP_Monitoring_Well_Design.pdf). Accessed on 1/20/10.
- DTSC. 2004. Guidance Document for the Implementation of United States Environmental Protection Agency Method 5035: Methodologies for Collection, Preservation, Storage, and Preparation of Soils to be Analyzed for Volatile Organic Compounds. November.
- DTSC. 2005. Interim Final Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air. December 15, 2004, Revised February 7, 2005.
- Fetter, C.W. 2000. "Applied Hydrogeology." Fourth Edition, Prentice Hall, Inc., ISBN-13: 9780130882394.
- Howard, Amster K. 1986. *Visual Classification of Soils, Unified Soil Classification System*, Geotechnical Branch Training Manual No. 5, Geotechnical Branch, Division of Research and Laboratory Services, Engineering and Research Center, US



- Bureau of Reclamation, Denver, CO. (Order from Bureau of Reclamation, Engineering and Research Center, Attention Code D-822A, P.O. Box 25007, Denver, CO 80225).
- The Interstate Technology & Regulatory Council (ITRC). 2002. Passive Diffusion Bag Samplers, Frequently Asked Questions. February.
- ITRC. 2004. Technical and Regulatory Guidance for Using Polyethylene Diffusion Bag Samplers to Monitor Volatile Organic Compounds in Groundwater. February.
- ITRC. 2007a. Protocol for Use of Five Passive Samplers to Sample for a Variety of Contaminants in Groundwater. February.
- ITRC. 2007b. Vapor Intrusion Pathway: A Practical Guide. January.
- Johnson, P.C. and R. Ettinger. 1991. Model for Subsurface Vapor Intrusion into Buildings.
- Kaminski, David. 2003. Go with the Flow. Low-flow sampling techniques improve sample quality and reduce monitoring program costs. *Water Well Journal*. June. pp. 24-28.
- Leeder, M.R. 1973. *Fluvialite fining upward cycles and the magnitude of paleochannels*. *Geology Magazine* 110, pp. 265 to 276.
- LeRoy, L.W. and D.O. LeRoy. 1987. *Subsurface Geology, Petroleum, Mining, Construction*, Fifth Edition, Colorado School of Mines, Golden, CO ISBN 0-918062-68-3.
- Los Angeles Regional Water Quality Control Board (LARWQCB)/DTSC. 2003. Advisory – Active Soil Gas Investigations. January 28.
- Massachusetts Department of Environmental Protection [MADEP]. 2002. Indoor Air Sampling and Evaluation Guide. April.
- McKee, E.D. and G.W. Weir. 1953. *Terminology for stratification and cross-stratification in sedimentary rocks*. *Geological Society of America Bulletin* 64, pp 381 to 390.
- Miller, Raymond W. and Roy L. Donohue. 1990. *Soils in Our Environment*, Seventh Edition, Prentice Hall, Englewood Cliffs, NJ, ISBN 0-13-095804-4.
- Morrison, R.D. and B.L. Murphy, eds. 2006. *Environmental Forensics: Contaminant-Specific Guide* (especially Chapter 6 by Lundegard, Chapter 15 by Boehm, Chapters 16 and 17 by Wang, and Chapter 18 by Stout, et al.). Academic Press/Elsevier, ISBN 13:978-0-12-507751-4.
- Murphy, B.L. and R.D. Morrison, eds. 2002. Introduction to Environmental Forensics (especially Chapter 5 by Philip and Chapter 6 by Stout, et al.). Academic Press, ISBN 0-12-511355-2.
- New York State Department of Health [NYSDOH]. 2005. Indoor Air Sampling and Analysis Guidance. February 1.
- Nielsen, David M., ed. 2006. Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring, Second Edition. CRC. January 2006.
- Powers, M.C. 1953. *A new roundness scale for sedimentary particles*. *Journal of Sedimentary Petrology* 23, pp. 830 to 847.
- Puls, R.W. and M.J. Barcelona. 1996. Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures. EPA Ground Water Issue. EPA/540/S-95/504. April.
- Rahn, Perry H. 1996. *Engineering Geology, an Environmental Approach*, Second Edition, Prentice Hall PTR, Upper Saddle River NJ, ISBN 0-13-177403-4.
- Reading, H.G. (editor). 1978. *Sedimentary Environments and Facies*, Elsevier, NY, ISBN 0-444-00276-6
- Regional Water Quality Control Board (RWQCB) - North Coast. 2009. Vapor Intrusion Guidance Document. July.
- Reynolds, S.D. and D.A. Zemo. 1992. Methodology for the In-Field Design of Monitoring Wells in Heterogeneous Fine-Grained Formations. In: Current Practices in Ground Water and Vadose Zone Investigations, ASTM Special Technical Publication No. 1118.
- Tearpock, D.J. and R.E. Bischke (1991). *Applied Subsurface Geological Mapping*, Prentice Hall, Englewood Cliffs, NJ, ISBN 0-13-859315-9.

- U.S. Environmental Protection Agency (USEPA). 1991. Handbook of Suggested Practices for the Design and Installation of Ground Water Monitoring Wells. Allers, et al. EPA/600/4-89/034. NTIS #PB90-159807.
- USEPA 1992. Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies. EPA/600/R-92/128. July.
- USEPA. 1997. Expedited Site Assessment Tools for Underground Storage Tank Sites – A Guide for Regulators. EPA 510-B-97-001. March. <https://www.epa.gov/oust/pubs/sam.htm>
- USEPA. 1999. Region 9 Laboratory, Field Sampling Guidance Document #1205, Soil Sampling. September.
- USEPA. 2000. Sampling and Analysis Guidance and Template. Region 9. April.
- USEPA. 2002a. Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers, Ground Water Forum Issue Paper, Douglas Yeskis and Bernard Zavala, EPA 542-S-02-001. May.
- USEPA. 2002b. Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). Office of Solid Waste and Emergency Response, USEPA Publication No. EPA530-D-02-004. November.
- USEPA. 2005. Groundwater Sampling and Monitoring with Direct Push Technologies. OSWER Publication No. 9200.1-51; EPA 540/R-04/005. August 2005.
- USEPA. 2007. Region 4 and the Science and Ecosystem Support Division (SESD) Operating Procedure, Soil Sampling. November.
- Zemo, D.A. 2009. Suggested methods to mitigate bias from nondissolved petroleum in groundwater samples collected from the smear zone. Ground Water Monitoring & Remediation, Vol. 29, No. 3: 77-83.

### Further Reading.

- Aller, L., T.W. Bennett, G. Hackett, R.J. Petty, J.H. Lehr, H. Sedoris, D.M. Nielsen, and J.E. Denne. 1989. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. EPA/EMSL-Las Vegas, USEPA Cooperative Agreement CR-812350-01, EPA/600/4-89/034, NTIS #PB90-159807.
- American Society of Testing and Materials (ASTM). 2004. Standard practice for design and installation of ground water monitoring wells in aquifers. D 5092-04.
- ASTM. 2005. Standard guide for decommissioning of ground water wells, vadose zone monitoring devices, boreholes, and other devices for environmental activities. D 5299-99 (2005).
- California Department of Toxic Substances Control. 1995. Monitoring Well Design and Construction for Hydrogeologic Characterization: Guidance Manual for Ground Water Investigations. July. Available at: [http://www.dtsc.ca.gov/SiteCleanup/upload/SMP\\_Monitoring\\_Well\\_Design.pdf](http://www.dtsc.ca.gov/SiteCleanup/upload/SMP_Monitoring_Well_Design.pdf). Accessed on 1/20/10
- International Society of Environmental Forensics (ISEF) publishes a quarterly peer-reviewed journal, Environmental Forensics.
- Nielsen, David M., ed. 2006. Practical Handbook of Environmental Site Characterization and Ground-Water Monitoring, Second Edition. CRC. January.

# Laboratory Analysis and Methods

## Soil and Groundwater



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### Scope of This Chapter

The scope of this chapter is to introduce the analysis and laboratory methods for analyzing soil, groundwater, and soil vapor at petroleum hydrocarbon release sites in the State of California.

### Introduction

The purpose in analyzing samples of environmental media (i.e., soil, groundwater, soil vapor) is to acquire quantitative information (concentrations) regarding the petroleum hydrocarbon constituents and related chemicals (e.g., fuel additives) at a LUFT site. These data are then used to assess the lateral and vertical extent ("distribution") of petroleum constituents, and to assess risk to human health, safety, and environment posed by the petroleum constituents.

This chapter of the LUFT Manual describes the suggestions for analysis of soil, groundwater, and vapor including possible analytes and analytical methods. The analytical suggestions herein are presented as current "best practices" and, therefore, some analytes and methods are different from those contained in regional or local guidance documents which may pre-date this Manual.

For many years, California and other states have had very different approaches to analytical requirements for petroleum release sites due largely to trying to address the complexity of petroleum fuel mixtures. The scientific community has known for more than 15 years that the vast majority of risk posed to human health and water quality is driven by the aromatics benzene, toluene, ethylbenzene, xylenes (BTEX; but benzene in particular) and the oxygenate methyl tertiary butyl ether (MTBE). The BTEX compounds have relatively high toxicity and are the hydrocarbon constituents with the highest effective solubility in gasoline. MTBE has very high effective solubility, has relatively low biodegradation potential, and therefore creates longer plumes. MTBE has lower toxicity than benzene, but it has a low taste and odor threshold, therefore its California Maximum Contaminant Level (MCL) is low as well. While the rest of the hydrocarbons make up the majority of the mass in the product that may be present, they account for very little risk posed to human health or groundwater quality due to their lower toxicity and/or lower mobility in the environment.

In the late 1980s, the original California LUFT Manual required the use of a "total petroleum hydrocarbons" (TPH) analysis to attempt to "screen" for these other hydrocarbons. Over the past 20 years, the scientific community has learned that the use of a TPH analysis correlates poorly with the protection of human health or water quality, because the nature of the hydrocarbons in the TPH changes dramatically over time due to weathering. The individual constituents are not identified by the TPH analysis.

Some states have adopted a sophisticated "fractionated" TPH analysis, where the hydrocarbons are separated into aliphatic and aromatic fractions and then are subdivided into various selected carbon ranges. This analysis was developed to provide a scientific basis for using TPH in assessing risk quantitatively. However, what has been observed in states that have been using this approach is that the risk to human health and water quality from releases at LUFT sites is still usually controlled by BTEX and a few other discrete constituents.

Based on these facts, the analytical program recommended for LUFT sites is described below and is shown on Table 9. These analytes capture the vast majority of risk posed to human health and water quality from releases at LUFT sites.

**Important!** GeoTracker's uploading criteria require that laboratory data be uploaded according to the GeoTracker Electronic Deliverable Format (EDF). See the GeoTracker chapter of the Manual and the link below.  
[http://www.swrcb.ca.gov/ust/electronic\\_submittal/docs/edf\\_gr\\_v1\\_2i.pdf](http://www.swrcb.ca.gov/ust/electronic_submittal/docs/edf_gr_v1_2i.pdf)

## Analytes by Source Fuel Type for Soil and Groundwater

### Gasoline

Based on the chemistry of gasoline (described in the [Fate and Transport](#) chapter of this Manual, the suggested analytes for soil and groundwater samples at gasoline release sites are the following discrete constituents:

- The mono-aromatics: BTEX
- Naphthalene
- Oxygenates: MTBE and *t*-butyl alcohol (TBA)
- The lead scavengers: 1,2-dichloroethane (EDC) and 1,2-dibromoethane (EDB) should also be included in the analytical suite if the gasoline release was pre-1992.

In most LUFT site settings, organic lead is not persistent unless free product (LNAPL) is present; therefore, it is not necessary to routinely analyze for organic lead unless site-specific information suggests that free product could be present. If organic lead is found, it should be speciated to identify the alkyl species present. It is not necessary to analyze soil at LUFT sites for inorganic lead; decades of empirical data show that the inorganic lead concentrations that could plausibly result from the conversion of organic lead are usually not significantly above background.

### Diesel, Jet Fuel, and Other Fuel Oils

Based on the chemistry of diesel and other middle distillate fuels (discussed in the [Fate and Transport](#) chapter of this Manual, the suggested analytes for soil and groundwater samples at jet fuel, diesel, or other fuel oil release sites are the following discrete constituents:

- BTEX
- Naphthalene, and
- For fuels heavier than diesel #2, the priority pollutant polycyclic aromatic hydrocarbons (PAHs).

Regarding the PAHs, it is suggested that jet fuel and diesel releases be analyzed for naphthalene only, because empirical data indicate that naphthalene is the only PAH that is likely to be present in these fuels in concentrations high enough to be a potential threat to human health or groundwater quality. The other PAHs are typically not present in jet fuel or diesel #2 at concentrations significant enough to pose a threat.

### Waste (Used) Motor Oils

Fresh lubricating (motor) oils are composed primarily of C25 to C32 hydrocarbons, which are almost exclusively the branched and cyclic alkanes. The aromatic hydrocarbons are not present in these products before they are used in engines. Because of their very large molecule sizes and the fact that they are predominantly aliphatic, these unused oils are virtually insoluble in groundwater, are not volatile, and pose virtually no risk to human health.

However, when lubricating oils are used in engines, they pick up fuel components due to cross-leakage in the chambers and, often, trace concentrations of metals from engine wear. Waste motor oils are typically contained in a waste oil tank, which can also contain waste cleaning products used at the service station (e.g., solvents). Therefore, the suggested analytical suite for soil and groundwater in the case of a waste motor oil release is:

- BTEX,
- The 16 priority PAHs,
- Chlorinated solvents (which will include EDB and EDC), and
- Oxygenates: MTBE and TBA
- For soil only: analyze for the five "wear metals" (Cadmium, Chromium, Nickel, Lead, and Zinc) is suggested.

## Analytical Methods for Discrete Constituents

The volatile analytes BTEX, naphthalene, EDC, EDB, and the oxygenates (MTBE and TBA) are suggested to be quantified by U.S. Environmental Protection Agency (EPA) Method 8260B because this method uses gas chromatography-mass spectrometry (GC-MS). Other GC-photo-ionization detector/flame ionization detector (GC-PID/GC-FID) methods (e.g., EPA Method 8020) have been used in the past, but are not presently recommended because they can result in false positives or misquantifications due to peak interferences and the lack of mass-spectrometer identification. At the time of this writing, the LUFT Program has not formulated its response to the May 2010 recommendation from EPA that groundwater samples be analyzed for EDB using EPA Method 8011.

The 16 priority pollutant PAHs are suggested to be quantified by EPA Method 8270C Single Ion Monitoring (SIM) because it is a GC-MS method and can achieve the low detection limits required for human-health risk assessment. Although there are other methods which may be used for PAHs, they aren't presently recommended because they can result in misquantifications due to peak interferences (e.g., Method 8310) or they have detection limits that are often unacceptably high (e.g., Method 8270C). If a sample is analyzed using both EPA 8260 and EPA 8270 SIM, naphthalene will be analyzed twice. Use the higher of the reported concentrations for risk assessment or comparison to water-quality objectives (WQOs).

It is suggested that organic lead be quantified and speciated using GC-electron capture detector (ECD).

The analytes and analytical methods for soil and groundwater samples at LUFT sites are summarized in Table 9

**Table 9 – Analytes and Methods for Soil and Groundwater Samples at LUFT Sites**

Source Fuel/Product Type	Analytes	Analytical Method	Comments
Gasoline	BTEX, naphthalene, MTBE, TBA (plus EDC, EDB for pre-1992 release)	EPA 8260B	
Jet A/JP5/JP8, Diesel #1 or #2	BTEX, naphthalene	EPA 8260B	
Heavier Fuel Oils (Fuel oil #4, marine diesel, bunker fuel, etc.)	BTEX, naphthalene, 16 priority pollutant PAHs	EPA 8260B, EPA 8270 SIM	PAHs only for fuels heavier than Diesel #2
Waste (Used) Motor Oil	BTEX, naphthalene, chlorinated VOCs, MTBE, TBA	EPA 8260B	
	16 priority PAHs	EPA 8270 SIM	
	Wear Metals: Cadmium, Chromium, Nickel, Lead, Zinc	EPA 6020/200.8	Soil only

### Notes:

BTEX Benzene, toluene, ethyl benzene, and xylene  
 EDB 1,2-dibromoethane  
 EDC 1,2-dichloroethane  
 Jet A Commercial jet fuel  
 JP5 Jet Propellant 5, military jet fuel  
 JP8 Jet Propellant 8, military jet fuel  
 PAH Polycyclic aromatic hydrocarbon  
 TBA *t*-Butyl alcohol  
 VOC Volatile organic compound

- 1) Samples to be analyzed for lead scavengers only if release is pre-1992. If age of release is unknown, analyze for both oxygenates and scavengers.
- 2) 16 priority pollutant PAHs = naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorene, chrysene, fluoranthene, pyrene, benzo(b)fluoranthene, benzo(a) pyrene, benzo(k)fluoranthene, benzo(a)anthracene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene.

## Discussion Regarding Total Petroleum Hydrocarbons (TPH) Analysis

Analysis of “bulk” TPH (such as analytical method EPA 8015) for the assessment of human health risk or threat to water quality is not recommended at LUFT sites. The reason for this is that human health and environmental risk is almost always driven by the individual (discrete) constituents (discussed in the previous sections), and the TPH analysis does not provide information about these constituents, as discussed below.

In the early 1990s, the total recoverable petroleum hydrocarbons (TRPH) analysis (EPA Method 418.1) was replaced by EPA Method 8015 (“total petroleum hydrocarbons” or TPH), performed using GC-FID. EPA Method 8015 is an aggregate analysis that quantifies the total amount of organic compounds present in a sample over a selected carbon range. Petroleum hydrocarbons may, or may not, be present in the sample because the FID is not specific to petroleum and a sample cleanup (like silica gel cleanup) is not part of the method. EPA Method 418.1 included a silica-gel cleanup, so it measured only petroleum hydrocarbons. Another problem with these TPH methods is that they do not provide information about which individual constituents, or hydrocarbon classes, are present in the sample. Decades of empirical site data have shown that EPA Method 8015 concentrations are poorly correlated with risk to groundwater quality or to human health. This is because weathering of the released petroleum significantly changes the constituents which are present in the “TPH”; however, Method 8015 does not provide enough information to evaluate the composition of the release.

It is well known that the potential risk to groundwater or human health posed by petroleum is controlled by hydrocarbon molecular class (aromatic **vs.** aliphatic) and molecular size (carbon number) (Total Petroleum Hydrocarbons Criteria Working Group [TPHCWG] 1997). EPA Method 8015 provides some rudimentary information about molecular sizes, but it does not provide molecular class information. As such, it has limited utility, even as a screening tool. Although Method 8015 is a relatively inexpensive analysis, its use in California since the early 1990s as a screening or decision-making tool has resulted in significant expenditures which are, ultimately, not correlated with a reduction in risk. Therefore, due to analytical imprecision and poor utility even as a risk screening tool, bulk TPH methods are not recommended to be included in the standard suite of analytical methods used for assessment of risk or threat to water quality. However, the TPH analysis can be used for the evaluation of bulk product mobility (flow as a separate phase liquid due to gravity) and calculation of mole fraction or mass fraction of the discrete constituents for fate and transport calculations.

If analysis for TPH is performed, for example, to better characterize site-specific mass fractions of the BTEX compounds and their associated effective solubilities, the following section presents “best practices” analytical suggestions.

### Gasoline-Range Organics (GRO) Using Method 8015 or 8260B

Soil and groundwater samples can be analyzed for gasoline-range organics (GRO) by purge-and-trap using either EPA Method 8015M (modified) or EPA Method 8260B and quantified using a gasoline standard. Quantitative results from these two methods may not be comparable; therefore, it is recommended that one or the other be used at a single site, and that the method not be changed during a groundwater monitoring program. To capture the bulk of the gasoline range and also avoid overlap with the diesel range, the suggested carbon range for GRO quantification is C4 to C12. Chromatograms of samples, standards, and method blanks should be provided with the complete laboratory report.

### Diesel-Range and Oil-Range Organics (DRO/ORO) Using Method 8015

Diesel-range and oil-range organics (DRO and ORO) can be analyzed using EPA Method 8015M. This extraction-based method provides some information about the carbon sizes present in the sample. The gravimetric methods such as EPA Method 418.1 (TRPH) and EPA Method 1664 (hexane-extractable material) are not advised, because they provide virtually no information about the carbon ranges present. The suggested carbon range for quantification of DRO is C12 to C22, quantified using a diesel fuel standard. The reported results should include the total concentration, and that total concentration can be divided into two carbon-chain increments (C12 to C16 and C17 to C22). The carbon ranges are confirmed with *n*-alkane standards. These carbon-chain subdivisions can provide the basis for assumed potential toxicity factors or physical properties required for analysis of risk. The suggested carbon range for ORO is C23 to C32, quantified using a motor-oil standard. Chromatograms of samples, standards, and method blanks should be provided with the complete laboratory report.

Soil samples can be analyzed for DRO/ORO, but this method is not recommended for groundwater samples. Research has shown that the hydrocarbon constituents which would comprise the dissolved phase from a petroleum release are primarily BTEX, the C9 to C11 alkylbenzenes, and the C10 to C14 PAHs, depending on the source fuel type. These hydrocarbons would be quantified primarily within the GRO range (C4 to C12) and not the DRO range (C12 to C22). The



ORO analysis is inappropriate for groundwater samples, because none of the dissolved petroleum hydrocarbons would be within that carbon range (C23 to C32). If very much DRO or ORO is found in groundwater, it is an indication that a non-dissolved component (e.g., LNAPL) may have been included in the sample. For weathered releases, it is well established that the DRO/ORO quantification for groundwater samples reflects primarily polar non-hydrocarbons resulting from biodegradation of the petroleum, and not the dissolved petroleum hydrocarbons (Zemo and Foote 2003; Lundegard and Sweeney 2004). The expense of the DRO/ORO analysis for groundwater samples is often not justified because of the analytical imprecision and the ability to adequately evaluate the dissolved phase using GRO.

Samples analyzed by EPA 8015M for DRO/ORO can be extracted using either methylene chloride or hexane. Because the purpose of the analysis is to quantify the petroleum hydrocarbons in the sample, and not to simply quantify all of the extractable organics, hexane is the preferred extraction solvent. The extraction solvent should be noted on the lab report because the extraction solvent will likely impact the quantitative results, especially for weathered petroleum.

Soil samples can be extracted using EPA Method 3550. If groundwater samples are to be analyzed, they can be extracted using EPA Methods 3510, 3520, or 3511.

As discussed below, it is suggested that the extracts be cleaned up with silica gel to remove or reduce the polar non-hydrocarbons that may be present in the extract so that only the petroleum hydrocarbons are analyzed.

In an effort to use fewer resources and create less waste, the State of California is seeking improvements to the DRO/ORO analysis so that a smaller sample volume and less extraction solvent is used. For example, the use of 3511/8015 would allow for collection using Volatile Organic Analysis (VOA) vials instead of 1-liter amber bottles, and would only use 5 milliliters (mL) of hexane per sample, rather than 200 mL of methylene chloride. At the time of this writing, several laboratories were investigating different extraction methods and solvents in side-by-side studies with conventional methods. These new methods may be added in the future.

### Silica Gel Cleanup for DRO/ORO

The purpose of the DRO/ORO analysis is typically to provide quantitative data regarding the petroleum hydrocarbons present in soil or groundwater. These data are then compared to petroleum-based cleanup criteria or water quality objectives. Research performed since the mid-1990s has shown that, without silica-gel cleanup, analysis by EPA Method 8015 DRO/ORO is a “total extractable organics analysis” (not a TPH-specific method) and the results can include polar non-hydrocarbons if present in the soil or groundwater. These polar compounds typically result from the intrinsic biodegradation of the petroleum or they can be naturally occurring (Zemo and Foote 2003). The DRO/ORO analysis with a silica-gel cleanup removes or significantly reduces the polar non-hydrocarbons and provides the data necessary to assess the petroleum in the sample.

It is suggested that the 3510, 3520, and 3550 extracts be cleaned up using a silica-gel column (based on EPA Method 3630C, and using the appropriate rinse solvent) prior to analysis to minimize the polar non-hydrocarbons which may be present in the extract. For hexane extracts from the micro-extraction procedure (Method 3511), silica gel cleanup can be accomplished by adding a few grams of silica gel to the vial and shaking (e.g., as per EPA Method 418.1). However, data indicate that, for methylene chloride extracts, a column cleanup is much more effective for isolating petroleum hydrocarbons.

The State Water Resources Control Board (SWRCB), the San Francisco Bay Regional Water Quality Control Board (SFRWQCB), and DTSC’s Hazardous Materials Laboratory have recognized the technical issue of the inclusion of polar biodegradation by-products when analyzing water samples for TPH, and have issued guidance that specifically recommends the use of silica-gel cleanup to isolate the petroleum hydrocarbons from the biodegradation by-products when the objective is to measure the petroleum hydrocarbons (SWRCB 2002; DTSC HML 1999; SFRWQCB 1999).

The issue of polar non-hydrocarbons is discussed in more detail in the [Fate & Transport](#) chapter.

Additionally, silica gel cleanup of DRO/ORO extracts will provide data that better correlate with aliphatic/ aromatic fractions (if used), because the extracts are fractionated on a silica gel column and should not contain polar compounds.

**Important!** No matter what cleanup procedure is used, the laboratory control samples must demonstrate that the polar compounds have been adequately removed (e.g., by a reverse surrogate such as capric acid) and that the hydrocarbons are adequately retained (e.g., by a fresh diesel spike or a discrete hydrocarbon spike) in the cleaned-up extract.

### ***If Quantitative Risk Assessment of “TPH” Is Necessary***

If it is necessary to quantitatively assess risk associated with TPH, a fractionated TPH analysis is recommended. A fractionated TPH analysis provides information regarding both the size and the class of compounds present (e.g., aliphatic **vs.** aromatic hydrocarbons). These analyses are more expensive than EPA Method 8015M, but provide much more detailed information about the petroleum mixture, which is needed for fate-and-transport estimates and human-health risk calculations for TPH. Having these detailed data allows for the development of site-specific cleanup goals which eliminate reliance on conservative screening levels that are based on assumed molecular classes and molecular sizes found in TPH. It is anticipated that only a few representative samples would be collected and analyzed for fractionated TPH.

Several states have developed their own fractionated TPH analytical methods. These analyses are usually based on the Massachusetts Department of Environmental Protection (MADEP) Volatile Petroleum Hydrocarbons (VPH)/Extractable Petroleum Hydrocarbons (EPH) methods (MADEP 2004) or the TPH Criteria Working Group method (TPHCWG 1997).

**Important!** Because the MADEP VPH/EPH method has been used for more than 10 years as of this writing (with the most recent update in 2004), and because the method and corresponding quality assurance/quality control protocols (QA/QC) are readily available, this is the preferred method for fractionated TPH analysis performed for the LUFT program, at least until such time as Cal/EPA adopts or develops its own analytical method. The MADEP VPH/EPH will be modified slightly for the LUFT program, as discussed below.

The fractionation process is sensitive to analyst experience, but the benefit of having the fractionated data outweighs the potential for analytical error. California laboratories should use the QA/QC parameters from the MADEP methods.

The LUFT fractions for VPH (to be used for gasoline releases) are:

- Aliphatics: C5 to C8,
- Aliphatics: C9 to C12, and
- Aromatics: C9 to C10.

The LUFT fractions for EPH (to be used for jet fuel, diesel and heavier product releases) are shown here.

#### **Aliphatics:**

- C9 to C12,
- C12 to C16,
- C16 to C21,
- C21 to C32.

#### **Aromatics:**

- C9 to C12,
- C12 to C16,
- C16 to C21,
- C21 to C32.

These carbon-range fractions are consistent with most other states. If VPH/EPH analyses are to be performed, n-hexane (for gasoline releases) and 2-methylnaphthalene (for jet fuel and heavier product releases) should be added to the discrete constituent target analyte list. N-hexane and 2-methyl-naphthalene are the most toxic compounds in their respective carbon fractions. If they are not quantified separately from their fractions, it is common practice to assume that the entire C5 to C8 aliphatic fraction has the toxicity of n-hexane, and similarly that the entire C9 to C16 aromatic fraction is assumed to have the toxicity of 2-methyl-naphthalene. N-hexane can be analyzed using EPA Method 8260B, and 2-methylnaphthalene can be analyzed using either Method 8260B or 8270SIM.

In Massachusetts, when the VPH/EPH methods are used, the individual fraction concentrations are corrected or adjusted by subtracting out the concentrations of the applicable discrete target compounds (such as the BTEX compounds) before reporting the final concentrations. For the CA LUFT program, however, the MADEP VPH/EPH Methods will be modified to include the LUFT target compounds (the “discrete constituents,” above). It will be the responsibility of the risk assessor to



subtract out the concentrations of the compounds that are quantified in discrete analytical methods (Method 8260B or Method 8270 SIM).

It is expected that most sites will be characterized using VPH or EPH, but not both, unless a mixed plume is present. If a single sample has both VPH and EPH data, the EPH data should be used in the risk assessment for fractions C9 or larger so that there is not double-counting of overlapping carbon ranges.

### Special Handling for Turbid Groundwater Samples

The objective of analyzing groundwater samples is typically to determine the concentrations of dissolved petroleum in the groundwater because this is the mobile portion of the petroleum, and water quality objectives are based on dissolved concentrations. It is straightforward to measure the dissolved phase concentrations when the samples contain low turbidity (i.e., they were collected from properly developed monitoring wells). However, samples are frequently submitted to the laboratory containing turbidity or sheen, either from poorly-developed wells or from grab-groundwater screening samples collected from borings.

For sample locations within the smear zone, the sheen and any petroleum-affected soil particles provide a non-dissolved component (LNAPL, or free product) included within the groundwater sample. These samples have been proven to produce unrepresentative data, because the non-dissolved component is quantified in addition to the dissolved component (e.g., Zemo 2009).

#### Groundwater Sampling Tip:

When sampling groundwater, every effort should be made in the field to produce low-turbidity samples, including using pre-pack screens for open boring samples, redeveloping monitoring wells, low-flow purge and sampling, etc.

In cases where turbid samples or samples with sheen are collected and sent to the laboratory, attempts at reducing the impact of turbidity/sheen at the laboratory may provide higher-quality data. To focus on the dissolved constituents, turbidity may be reduced and the sheen removed or avoided by the laboratory before the sample is purged or extracted.

When focusing on volatile constituents and VPH or GRO, the samples can be centrifuged or gravity-separated in the VOA vial. For semi-volatile constituents and EPH or DRO, the samples can be filtered (0.7-micron glass-fiber TCLP filter), centrifuged, or gravity-separated in a separatory funnel. It has been demonstrated that the glass-fiber filter (the same as that used in the EPA TCLP analysis) does not significantly sorb dissolved petroleum hydrocarbons and therefore is recommended (Foote, et al. 1997; Lundegard and Sweeney 2004); other filter materials may sorb dissolved petroleum hydrocarbons and are not acceptable. After these procedures, the laboratory can subsample the water phase prior to purging or extraction.

Implementing these turbidity-reduction measures will result in reported concentrations which better represent dissolved-phase petroleum in the groundwater as opposed to sheen or petroleum adhered to the soil particles. However, the sample may still include non-dissolved petroleum due to the physical limitations of these laboratory handling methods.

# Laboratory Analysis and Methods

## Soil Vapor

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In soil vapor, components of gasoline, jet fuel, and diesel can be analyzed using modifications of EPA Methods 8260B, TO-15, and/or TO-17, depending on the detail and detection limits needed. The advantage of these methods is that they provide for mass spectrometry (MS) identification, unlike Method TO-3, which uses GC-FID.

**Table 10 – Analytes for Soil Vapor Samples at LUFT Sites** (Modified EPA Methods 8260B, TO-15/17)

MTBE
BTEX
Naphthalene
1,2-Dichloroethane (EDC)
1,2-Dibromoethane (EDB)

Notes:

BTEX: benzene, toluene, ethylbenzene, xylenes

MTBE: methyl tertiary butyl ether

In addition to the petroleum-related constituents, it is recommended that soil-vapor samples also be analyzed for the leak detector compound and for oxygen and carbon dioxide (by American Society for Testing and Materials [ASTM] D-1946). It may be prudent to also analyze for methane if light non-aqueous-phase liquid (LNAPL, free product) is known or believed to be present.

Based on all available data, the target analytes recommended here capture the vast majority of risk posed by vapors from releases at LUFT sites, and there is usually no technical reason to use a “TPH” analysis for vapor samples.

### If Risk Assessment of “TPH” in Vapors Is Necessary

If a risk assessment of the TPH in soil vapor is necessary, the MADEP air-phase petroleum hydrocarbons (APH) method (based on TO-15) is recommended. This is the best method to assess “TPH” risk from soil vapors because it is a fractionated analysis, which provides quantitative data regarding aliphatics and aromatics by carbon ranges.

The MADEP fractions for APH are:

- Aliphatics: C5 to C8,
- Aliphatics: C9 to C12, and
- Aromatics: C9 to C10.

These fractions are suggested for the LUFT program. If the APH method is used, n-hexane and 2-methylnaphthalene should be added to the discrete constituent target analyte list (Table 10) so toxicity of the respective fractions is not overestimated.

In certain cases, an analysis of bulk TPH in soil vapor may be desired; however, it is strongly recommended that bulk TPH measurements not be used for risk-assessment purposes. Bulk TPH in soil vapor can be analyzed by modified EPA Method 8260B or TO-15 (C4 to C12). Because both methods are GC-MS methods, they can be used to provide additional information about the constituents present by requesting “tentatively identified compound (TIC)” from the mass spectrometry data. Requesting TICs to be quantified is important, because the concentrations of hydrocarbons in the vapor phase of a petroleum release are expected to be dominated by the aliphatics, due to their high vapor pressure and relatively lower biodegradation potential as compared to the aromatics. The aliphatics have much lower toxicity than the aromatic compounds. If TICs are quantified by the lab, human health risk can be evaluated for the discrete compounds detected. The TPH analysis by modified EPA Method 8015 provides no information about the constituents actually present, and is not recommended for vapor samples.

**Important!** The MADEP Air-Phase Petroleum Hydrocarbons (APH) method (based on TO-15) is the preferred method for fractionated analysis of soil vapor for the LUFT program until Cal/EPA adopts or develops its own analytical method.

# Laboratory Analysis and Methods

## LNAPL



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Although the following analyses are not routinely performed on LNAPL samples, important information about the nature of the LNAPL can be obtained. This information can be used to improve the understanding of site conditions and to assist with remediation design.

### Physical Properties

The physical properties typically measured for LNAPL samples are: dynamic viscosity (ASTM D445), density (ASTM D1481), and surface and interfacial tension (ASTM D971). In addition to these tests on LNAPL itself, there are several types of tests that measure the relationship between the LNAPL and the soil that influence LNAPL mobility, such as: pore fluid saturation, capillary testing, and centrifugal force residual saturation (American Petroleum Institute [API] RP40, ASTM D6836, ASTM D425M).

### Chemical Composition

LNAPL samples can be analyzed for chemical composition using high-resolution GC-FID (ASTM D3328); high-resolution GC-MS (ASTM D5739); or simulated distillation (ASTM D2887). In addition, review of the readily available TPH chromatograms (which should be provided by the laboratory for EPA Method 8015 TPH as part of the data package) can provide information about product type and weathering. Forensic analyses are discussed in the next section.

**Further Reading.** See the Fate and Transport chapter of this Manual for additional information on physical and chemical properties of LNAPL.

# Laboratory Analysis and Methods

## Forensic Analysis

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### Purpose of Forensic Analysis

Forensic chemistry is typically used at LUFT sites to identify the product type, to distinguish between two or more product plumes, or to estimate the date of release. There are many forensic tools available for petroleum investigations. The best tool(s) for application to a particular case depend(s) on the question posed, so clarity about the ultimate objective of the forensic work is important.

Different forensic tools are better suited to different types of products or different sample media (product, soil, dissolved-phase in groundwater, or in vapor). Forensic interpretations regarding petroleum releases must also incorporate impacts of environmental weathering (by evaporation, biodegradation, or solubilization) and impacts of changes in crude oil sources or refinery processes, because these factors greatly influence the composition of the mixture.

Presently, the most commonly used forensic tools for petroleum releases are

- 1) Chromatogram pattern matching
- 2) Analyses of discrete constituents or families of constituents
- 3) Analyses for additives or blending agents
- 4) Biomarkers
- 5) Stable isotopes

All of these tools have wide acceptance in the forensics community, and peer-reviewed literature provides many examples of their applications. This section provides a brief introduction to each of these tools and comments on their uses in various sample media. Because the vast majority of petroleum constituents have low effective solubilities in water, the dissolved phase of crude oil and most other petroleum hydrocarbon products is limited to relatively few constituents, and is similar among sources. Therefore, while many of the classic forensic tools that were developed for oil or similar products can have utility for soil samples, they are not as useful for dissolved-phase groundwater plumes.

**Note.** It is important to note that forensic analyses are not “standardized,” but instead vary among laboratories. Most laboratories use modifications of existing ASTM or EPA SW-846 methods for their forensic analyses. Comparing data between two or more laboratories, therefore, can be challenging.

### Gas Chromatogram Pattern Matching

Gas chromatogram pattern matching has been used for many decades for product-type identification. The foundation of this tool is high-resolution gas chromatography (GC), which separates constituents within a sample based primarily on boiling point (most laboratories use modifications of ASTM D3328). This forensic technique relies primarily on matching the boiling range (carbon range) and the pattern of the peaks or “humps” on the chromatogram of the unknown compound when compared to those of known standards. The boiling ranges and general chromatographic character of most refined fuels or lubricating oils is widely agreed upon by forensic experts, and there are multiple examples in literature. The chromatographic character changes with environmental weathering of the petroleum, but in predictable ways. Chromatograms can also be used to characterize a mixture where multiple products have been released.

### Discrete Constituent Analyses and Constituent Ratios

Obtaining detailed information about the discrete petroleum constituents present in a sample is a useful tool for distinguishing between products of similar boiling ranges (e.g., “Is the product a mixture of gasoline and Jet A fuel, or is it a wide-cut jet fuel such as JP-4?”). For the gasoline-range and jet-fuel range products, the workhorse tool is the “PIANO” analysis, an acronym for Paraffins, Isoparaffins, Aromatics, Naphthenes (cycloalkanes), and Olefins. These five families of hydrocarbon molecules have differing properties and occur in products in differing proportions.

The PIANO analysis (ASTM D5134 or modified EPA Method 8260) quantitatively reports more than 100 hydrocarbons in the volatile range, usually up to C13 or C15. For the diesel-range and heavier products, the tools most frequently used are the “GC/MS Full Scan” (ASTM D5739), where six or more hydrocarbon families are isolated and compared qualitatively or quantitatively, and the “Extended PAH” analysis (modified EPA Method 8270 SIM), where typically up to 53 PAHs and sulfur-containing heterocyclics (e.g., dibenzothiophenes) are quantified. This includes the “parent” and alkylated PAHs of each homologous series (e.g., phenanthrene and the C1, C2, C3, and C4 phenanthrenes).

Ratios of the various PIANO components are routinely used to compare similarity among gasolines, and to potentially age-date products due to refining-process changes that significantly impact the PIANO signature. The relative proportions of the hydrocarbon families can be used to distinguish between diesels and heavier fuel oils and crude oils. The relative proportions of the extended PAHs are routinely used to distinguish petroleum sources from combustion sources (e.g., bunker fuel vs. creosote). Certain ratios of the alkylated PAHs can be used to compare similarity among petroleum sources. These tools are useful for product and soil samples, but can have less utility in dissolved-phase groundwater samples.

**Further Reading.** There is recent research into the PIANO type of analysis for forensic evaluation of soil-vapor samples by modifying EPA Method TO-15 (Stout, et al. 2006).

## Biomarkers

Biomarkers are “molecular fossils” where biochemicals such as sterols are transformed to biomarkers such as steranes during the geologic formation of crude oil. They reflect the crude-oil source from which the product was refined and are very resistant to weathering or refining effects. The biomarkers are typically analyzed as part of the “GC-MS Full Scan” (ASTM D5739), where the ion chromatograms are evaluated qualitatively. Some labs have developed a quantitative biomarker analysis based on a modification of EPA Method 8270 SIM. Biomarkers have been used for many years, and are routinely used to distinguish among petroleum sources, especially for crude oils and diesel-range or heavier products.

**Note.** Due to their low solubility (a consequence of their very complex molecular structure), biomarkers would not be useful in a dissolved-phase groundwater plume.

## Additives or Blending Agents

This forensic tool includes the alkyl lead packages (tetra ethyllead [TEL], tetra methyllead [TML], etc.) and lead scavengers (EDB, EDC) that were historically added to automotive gasolines, and oxygenates such as the ethers (MTBE, tertiary amyl methyl ether [TAME], etc.) and alcohols (TBA, ethanol) that have been blended with gasoline relatively recently. These constituents are routinely used for age-dating gasoline releases. Research has shown that the alkyl leads typically degrade relatively quickly in the environment outside of the product matrix. Additives or blending agents can be present in unexpected products as a result of cross-contamination during fuel transport and storage. Lead scavengers and oxygenates are soluble, and therefore can be useful for forensic evaluation of a dissolved-phase groundwater plume.

## Stable Isotopes

Stable isotopes of carbon, hydrogen, oxygen, and sulfur are forensic tools that are relatively new to application in environmental investigation settings. These isotopes are in the signature of the crude oil and therefore reflect the crude-oil source from which the product was refined. Bulk stable isotopes have been used for decades in the petroleum industry to characterize individual crude oils. Due to recent advances in analytical techniques, it is possible to analyze product, soil, groundwater, and vapor matrices for stable isotopes on either a “bulk” or “constituent-specific” scale. The peer-reviewed literature contains many examples of forensic and remediation applications for stable isotopes, especially constituent-specific applications. Caution must be used in forensic interpretations, because certain isotope ratios change due to biodegradation.

## References

- Footo, G.R., D.A. Zemo, S.M. Gallardo, M.J. Grant, B.T. Benson, and J.E. Bruya. 1997. Case study: Interferences with TPH analyses of grab groundwater samples, Chap. 3 in *Principles and Practices for Diesel Contaminated Soils*, vol. VI, ed. C.P. Barkon, P.T. Kostecki, and E.J. Calabrese, 27-39. Amherst, Massachusetts: Amherst Scientific Publishers.
- Lundegard, P.D. and R.E. Sweeney. 2004. Total petroleum hydrocarbons in groundwater – Evaluation of nondissolved and nonhydrocarbon fractions. *Environmental Forensics* 5: 85-96.
- Massachusetts Department of Environmental Protection (MADEP), May 2004. Revision 1.1, Method for the Determination of Volatile Petroleum Hydrocarbons (VPH).
- MADEP, May 2004. Revision 1.1, Method for the Determination of Extractable Petroleum Hydrocarbons (EPH).
- MADEP, December 2008. Final, Method for the Determination of Air Phase Petroleum Hydrocarbons (APH).
- State of California. 1989. Leaking Underground Fuel Tank (LUFT) Task Force. *LUFT Field Manual*. Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. October.
- Zemo, D.A. 2009. Suggested Methods to Mitigate Bias from Non-dissolved Petroleum in Ground Water Samples Collected from the Smear Zone. *Ground Water Monitoring & Remediation*, Vol. 29, No. 3: 77-83(7).

# Risk Evaluation and Risk Management

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## Scope of This Chapter

This chapter discusses the process of evaluating and managing risk at a LUFT site. It also provides LUFT-specific screening tools.

Using the results of a risk evaluation and a properly developed Conceptual Site Model (CSM) to make decisions about cleanup and corrective actions at a site is called “risk management.” This “risk-based” decision-making process is increasingly considered to be more appropriate and cost-effective than (yet still sufficiently protective as) decisions based either on “background” or “non-detectable” levels of constituents of concern (COCs) or on numerical criteria that have been developed without recognition of risk-assessment principles (Interstate Technology & Regulatory Council [ITRC] 2008).

Risk to human health, safety, and the environment should be considered at every phase of work at a LUFT site, from the initial discovery through the site-assessment and remediation phases. If, at any point, the CSM confirms the presence of a complete exposure pathway, evaluation of the risk associated with that pathway is necessary. The goal of the process is to ensure that management decisions for potentially impacted sites provide an adequate level of protection for human health, safety, and the environment.

Risk evaluation can be used to:

- Establish site-assessment objectives.
- Determine the need for additional site characterization.
- Determine the need for corrective action.
- Establish cleanup objectives and standards.
- Communicate with stakeholders.
- Determine the need for emergency or accelerated response.

The ITRC has developed two documents (referred to by ITRC as RISK-1 and RISK-2 [ITRC 2005, 2008]) regarding the use of risk assessment in the management of contaminated sites. These documents are highly recommended reading to learn more about how various state agencies and regulatory bodies apply risk assessment in the process of risk management. This chapter has borrowed some concepts from these documents to describe the process of risk management. Access the documents at:

<http://www.itrcweb.org/guidancedocument.asp?TID=44>

Risk can be evaluated in several different ways, but is often evaluated using a tiered approach in which the complexity of the evaluation increases with each tier (or step) in the process. The objective of this section of the LUFT Manual is to present a tiered approach to risk assessment (i.e., start simple and increase complexity, as necessary); however, it does not prescribe specific processes for the various “tiers.”

## Initial Risk Screening

The first step in the tiered process is one in which COC concentrations in site media (soils, groundwater, vapor etc.) are compared to conservative, regulatory-derived screening levels designed to be protective under a wide range of potential exposure conditions. These screening levels are developed using standard exposure assumptions and chemical toxicity criteria established by state and federal agencies. They are typically meant to be used at many different types of sites, ranging from small, relatively simple sites, such as LUFT sites, to large, highly complex sites, such as landfills. In order to address sites with potentially very large source areas, the commonly used initial risk screening levels are likely overly conservative for LUFT sites. Also, most of these screening levels are calculated assuming that each petroleum constituent occurs on its own and is not part of a mixture, and they do not incorporate biodegradation. Nevertheless, they are a good place to start in the risk-evaluation process. Agencies that have developed these screening values emphasize that the intended purpose of the values is for site screening and not for use as generic cleanup levels that must be attained at individual sites.



## Initial Screening Options

There are a number of options for initial screening levels to be used at LUFT sites, including Environmental Screening Levels (ESLs), Maximum Contaminant Levels (MCLs), and USEPA Regional Screening Levels (RSLs).

ESLs are developed by the Regional Water Quality Control Board (RWQCB) Region 2 – San Francisco Bay and presented in *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater* (Interim Final – May 2008). This report presents lookup tables for over 100 chemicals commonly found at sites with contaminated soil, groundwater and/or soil vapor. For any particular chemical, the lookup tables present multiple screening levels designed to be protective of human health, ecological receptors, drinking-water supplies, and general nuisance conditions. Care must be given to select the appropriate tables to screen LUFT sites, and to understand the assumptions made for the COCs that have been identified. For example, the direct-contact values for the individual COCs in soil may be appropriate, but the values for soil to protect groundwater or surface water do not incorporate effective solubility or biodegradation. Also, for non-carcinogens, the ESLs assume a target hazard index (HI) of 0.2 instead of 1.0 because they assume that five COCs are present which may be a very conservative assumption.

ESLs are available online at:

<http://www.waterboards.ca.gov/sanfranciscobay/esl.shtml>.

MCLs are legally enforceable standards developed by EPA and the State of California. MCLs correspond to the highest level of a contaminant that is allowed in drinking water. These values are typically used to screen potential drinking-water sources at LUFT sites, but are not applicable to non-drinking-water sources. California MCLs can be found online at:

<http://www.cdph.ca.gov/certlic/drinkingwater/pages/chemicalcontaminants.aspx> and EPA MCLs are online at: <http://www.epa.gov/safewater/contaminants/index.html>.

EPA RSLs are chemical-specific concentrations for contaminants in air, drinking water and soil that are considered to be protective for human health under assumed reasonable maximum residential or commercial/industrial exposure conditions. RSLs were initially developed for use in EPA's Superfund/Resource Conservation and Recovery Act (RCRA) programs and were previously issued as Region IX Preliminary Remediation Goals (PRGs) or Region III Risk-Based Concentrations (which they replaced in 2008). RSLs are available online at:

<http://www.epa.gov/region09/superfund/prg/index.html>.

The California Environmental Protection Agency (Cal/EPA) Office of Environmental Health Hazard Assessment (OEHHA) developed California Human Health Screening Levels (CHHSLs) as required by Senate Bill 32, the California Land Environmental Restoration and Reuse Act (passed in 2000). The CHHSL screening numbers are not intended for use by regulatory agencies with the authority to require remediation of contaminated soils (OEHHA 2005). Furthermore, they do not contain screening levels for volatile chemicals in soil (such as BTEX, MTBE, and TBA). For these reasons, CHHSLs may have limited application for LUFT sites.

Comparing concentrations of site-specific COCs to ESLs, MCLs, or RSLs is for initial risk-screening purposes. If adequate site assessment has been completed, then site concentrations below these levels indicate that further action is unlikely to be necessary to protect human health, safety, and the environment. Site concentrations exceeding these levels, however, do not necessarily indicate that the site presents a human health risk or a risk to the environment.

### **Options for Selecting Site Concentrations to be Compared to Screening Levels**

Comparing site data to screening levels for LUFT sites has often been based upon the highest concentration found in the source media. Making decisions based on a maximum measured concentration without considering a more realistic exposure-point concentration can result in expensive and/or unnecessary corrective action.

One option is to use an average source concentration for comparison to the screening levels rather than the maximum detected concentration. In this case, the average may be calculated using a 95 percent upper confidence level (UCL) of the mean (if there is adequate data). If the source is very small, areal averaging may be appropriate to estimate a more realistic exposure point concentration. For example, if the source is 2 meters (m) × 2 m in surface soil, the risk assessor may choose to average the concentration across a likely exposure area, such as the area of a small back yard.

## LUFT-Specific Risk Screening Tools

A set of LUFT-specific Risk Screening Tools has been developed for use in a second screening step. These screening tools are more directly applicable to LUFT sites, because they have been developed based on common exposure pathways and

environmental conditions typically seen at gasoline and diesel fuel release sites in California. For the vapor intrusion pathway, leaching to groundwater pathway, and cases where groundwater is already impacted, a series of non-concentration-based risk screening tools has been developed to evaluate whether or not the pathway is of concern from a human health perspective.

For the exposure pathways where site COC concentrations are found to exceed initial risk screening levels, the LUFT Risk Screening Tools could be used to further evaluate potentially complete exposure pathways, as demonstrated by the CSM. It is important to note that all of the LUFT Risk Screening Tools have been developed based on common conditions at LUFT sites. If the assumptions made by these LUFT-Specific Risk Screening Tools are not representative of site conditions, then the screening tools presented below may not be valid for that particular site, and site-specific risk evaluation may be appropriate.

The LUFT-Specific Risk Tools have been developed for the four most likely source and exposure pathway combinations described in the [CSM](#) chapter. These are:

- Direct contact with soil, including dermal contact, ingestion, and inhalation of dust and volatiles,
- Volatilization from soil or groundwater to indoor air,
- Leaching from soil to groundwater, and
- Groundwater already impacted above WQOs.

### **Direct Contact with Soil – LUFT Risk Screening Tool**

Numerical screening levels for direct contact with soil have been developed for the individual COCs identified for gasoline and diesel fuels: BTEX, naphthalene, MTBE, and TBA. It is assumed that the vast majority of the potential risk to human health and groundwater quality posed by gasoline and diesel is captured by these discrete constituents. Screening levels are not provided for PAHs larger than naphthalene because they are not present in gasoline or diesel in sufficient concentrations to pose a risk. The details of the screening level development and assumptions are discussed in Appendix A (please note the Appendix is undergoing per review and will be added after the release of the LUFT Manual for public comment).

As discussed in the [CSM](#) chapter, the potential exposure pathways for soil include ingestion of soil, dermal contact with soil, and inhalation of volatile and dust emissions. This group is often called the “direct contact” exposure pathways. The LUFT screening levels for this pathway under residential, commercial/ industrial land use scenarios, and for the construction/ utility worker scenario, are shown on Tables 11a and 11b.

A target risk level of  $1 \times 10^{-6}$  risk for carcinogens and an HI of 1.0 for non-carcinogens are assumed in all cases. These screening levels are designed to be applied to soils to a depth of 3 feet for residential and commercial/ industrial receptors. For residential land use, it is assumed that residents may come into contact with the soil between the ground surface and a depth of 3 feet (“surface soil”), which is the depth of typical gardening activities. For impacted soil at depths from 3 to 10 feet (a “swimming pool” or “septic system installation” scenario), it is assumed that the potential risk posed to residents by this soil is insignificant, because excavations by the homeowner to that depth would be rare (exposure frequency and duration are short), most of the petroleum-affected soil would be removed to create the swimming pool or septic system, and petroleum in soil would volatilize and biodegrade if it were placed at the ground surface. For commercial/industrial receptors, it is similarly assumed that commercial workers could contact the soil at depths between ground surface and 3 feet. For the case of a construction/utility trench worker, the relevant screening levels should be applied to soils at depths from 0 to 10 feet.

The screening levels in Table 11a assume reasonable maximum exposure (RME) conditions and that an infinite source of contaminants is present at the site, consistent with ESLs and RSLs used for initial risk screening. The main difference between the LUFT screening levels and the initial risk screening levels is the way in which the volatilization rate to outdoor air is calculated. Details are provided in Appendix A. Note that the LUFT screening levels in Table 11a still assume that the concentration at the beginning of the exposure remains constant throughout the exposure period for the ingestion of soil and dermal contact pathways.

The screening levels in Table 11b use the same exposure assumptions as used in Table 11a; however, the screening levels in this table assume that the source will be depleted over time. This is appropriate for LUFT sites at which the COCs are known to be very volatile and to biodegrade rapidly in the subsurface (both in groundwater and soil). The derivation of all screening levels presented in Tables 11a and 11b is described in detail in Appendix A.

**Table 11a**  
**LUFT Screening Levels for Soil:**  
**Direct Contact – Infinite Source Term**

<b>Land Use/Receptor</b>	<b>Benzene (mg/kg)</b>	<b>Toluene (mg/kg)</b>	<b>Ethylbenzene (mg/kg)</b>	<b>Xylenes (mg/kg)</b>	<b>MTBE (mg/kg)</b>	<b>TBA (mg/kg)</b>	<b>Naphthalene (mg/kg)</b>
<b>Residential</b> Soil depth 0 to 3 feet only	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>
<b>Commercial</b> Soil depth 0 to 3 feet only	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>
<b>Construction/Utility worker</b> Soil depth 3 to 10 feet	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>	<i>TBD</i>

**Notes:**

TBD = To Be Determined. These values will be supplied in an update to the DRAFT LUFT Manual.

mg/kg = Milligram per kilogram

MTBE = Methyl tertiary butyl ether

TBA = t-Butyl alcohol

- (1) See Appendix A for details on the derivation of these screening levels.
- (2) Assumes 10E-6 cancer risk and Hazard Index (HI) of 1.0 for all receptors.
- (3) For diesel release sites: If TPHd (or diesel-range organics [DRO]) data are available, these data can be used for screening instead of the individual naphthalene screening levels. Assuming a mass fraction of 0.26% naphthalene in unweathered diesel (Potter and Simmons 1998), the naphthalene screening concentrations could be exceeded only if the sample exceeded \_\_\_ mg/kg TPHd for residential; \_\_\_ mg/kg TPHd for commercial; or \_\_\_ mg/kg TPHd for the construction worker. If these TPHd values are exceeded for the respective receptor, then the sample should also be analyzed for naphthalene.

**Table 11b**  
**LUFT Screening Levels for Soil:**  
**Direct Contact – Source Depleting Due to Degradation**

<b>Land Use/Receptor</b>	<b>Benzene (mg/kg)</b>	<b>Toluene (mg/kg)</b>	<b>Ethylbenzene (mg/kg)</b>	<b>Xylenes (mg/kg)</b>	<b>MTBE (mg/kg)</b>	<b>TBA (mg/kg)</b>	<b>Naphthalene (mg/kg)</b>
<b>Residential</b> Soil depth 0 to 3 feet only	TBD	TBD	TBD	TBD	TBD	TBD	TBD
<b>Commercial</b> Soil depth 0 to 3 feet only	TBD	TBD	TBD	TBD	TBD	TBD	TBD
<b>Construction/Utility worker</b> Soil depth 3 to 10 feet	TBD	TBD	TBD	TBD	TBD	TBD	TBD

**Notes:**

TBD = To Be Determined. These values will be supplied in an update to the DRAFT LUFT manual.

mg/kg = Milligram per kilogram

MTBE = Methyl tertiary butyl ether

TBA = t-Butyl alcohol

- (1) See Appendix A for details on the derivation of these screening levels.
- (2) Assumes 10E-6 cancer risk and Hazard Index of 1.0 for all receptors.
- (3) For diesel release sites: If TPHd (or diesel-range organics [DRO]) data are available, these data can be used for screening instead of the individual naphthalene screening levels. Assuming a mass fraction of 0.26% naphthalene in unweathered diesel (Potter and Simmons 1998), the naphthalene screening concentrations could be exceeded only if the sample exceeded \_\_\_\_ mg/kg TPHd for residential; \_\_\_\_ mg/kg TPHd for commercial; or \_\_\_\_ mg/kg TPHd for the construction worker. If these TPHd values are exceeded for the respective receptor, then the sample should also be analyzed for naphthalene

### Vapor Intrusion Risk Screening Tool

Quantitative, risk-based soil screening levels for the volatilization to indoor air pathway (commonly known as the **vapor intrusion pathway**) have not been developed. Instead, the results of published empirical data and chemical fate-and-transport modeling regarding the natural attenuation of petroleum hydrocarbons in soil vapor and the potential for vapor intrusion were used to develop a series of screening steps to assess the potential for a particular LUFT site to present an unacceptable risk from this pathway.

Based on these studies, a LUFT site is assumed to present no unacceptable risk from vapor intrusion if the following site conditions are met:

- 1) *For soil sources and low-strength groundwater sources:* 5 feet or more of clean soil between the bottom of the building and the shallowest impacted soil or impacted groundwater.
- 2) *For high-strength groundwater sources:* 10 feet or more of clean soil between the bottom of the building and the shallowest impacted soil or impacted groundwater.
- 3) *For measurable free product on the water table:* 30 feet or more of clean soil between the bottom of the building and the water table.

A “low-strength groundwater source” is defined as *dissolved-phase* benzene groundwater concentrations below 1,000 micrograms per liter (µg/L) and *dissolved phase* TPH concentrations below 10,000 µg/L. A “high-strength groundwater source” is defined as dissolved concentrations of benzene greater than 1,000 µg/L and *dissolved-phase* TPH concentrations greater than 10,000 µg/L.

In the unsaturated zone, clean soil is defined as TPH concentrations less than 100 milligrams per kilogram (mg/kg), photo-ionization detector (PID) readings of less than 10 parts per million (ppm), or oxygen present concentrations >4%. Under

these conditions, it is assumed that natural attenuation is sufficient to mitigate concentrations of volatile petroleum constituents. Conversely, if these conditions do not apply at a particular LUFT site, a site-specific soil vapor intrusion and risk evaluation may be required.

### **Leaching from Soil to Groundwater Screening Tool**

This scenario assumes that COCs are present in the vadose-zone soil but have not reached groundwater. As with soil vapor, soil screening levels for the **leaching to groundwater pathway** have not been developed; rather, a simple fate-and-transport equation is used to estimate how much “clean” soil would be required to attenuate the leachate concentrations so that the leachate would meet California MCLs (or, in the case of MTBE, the California odor threshold). The details of the calculations are described in Appendix A (please note the Appendix is undergoing per review and will be added after the release of the LUFT Manual for public comment).

This evaluation demonstrates that, if there are more than 10 feet between soil impacted with BTEX or naphthalene and underlying groundwater, then it is assumed that the impacted soil cannot lead to COC concentrations in groundwater that would exceed WQOs. (Note: this distance is under peer review and may be updated when the appendix describing this pathway is released.) For MTBE and TBA, the distance is much greater, because these chemicals are very soluble and, in the case of MTBE, assumed to have lower degradation rates. Briefly, the calculation is based on the effective solubility concentrations for the COCs in fresh gasoline (diesel for naphthalene) and includes a conservative travel velocity and degradation assumptions.

### **Groundwater Already Impacted Above WQOs Screening Tool**

For this pathway, petroleum has migrated down to the capillary fringe/water table and dissolved-phase constituents have impacted groundwater above WQOs. Free product (LNAPL) or sheen may, or may not, be present at the water table at the source area. Risk management and protection of human health, safety, and the environment in this case are primarily focused on limiting plume migration (protecting un-impacted groundwater), protecting receptors, and restoring impacted groundwater to its beneficial use within a reasonable time frame.

Determining whether a groundwater plume from a LUFT release poses a significant threat to human health, safety, and the environment involves evaluating several factors. In 1996, most Regional Boards published their individual guidance documents for LUFT sites outlining factors that, when taken together, were considered protective of human health, safety, and the environment even though groundwater was impacted. Since that time, several Regional Boards have updated their guidance (e.g., Central Valley Regional Board 2004) and the State Water Resources Control Board (SWRCB) has issued closure letters consistent with these factors. These factors incorporate the role of natural attenuation of the COCs in plumes. Each Region’s guidance is slightly different, and the SWRCB’s language is slightly different again, but the main factors that are considered protective are similar enough to summarize here.

#### **1. The source, including mobile free product, has been removed or remediated.**

The “source” has been typically defined as mobile free product and residual (immobile) product trapped in the soil that has enough soluble or volatile constituents to pose a significant threat to groundwater quality or human health.

Free product is required to be removed “to the maximum extent practicable,” and “the abatement of migration shall be the predominant objective in the design of a free product system” [CCR 23, Division 3, Chapter 16, Section 2655(a) and (c)]. Therefore, evaluation of the potential for migration of the free product is important. This is typically achieved by monitoring the free-product plume for increases in measured thickness or increases in lateral extent over time. As discussed in the Fate and Transport chapter, product thickness measured in monitoring wells varies with changing water level elevation, and this factor must be included in the evaluation. In general, at a constant water level elevation, if the product thickness in individual wells does not increase or the footprint (lateral extent) of the free-product plume does not increase, the free product is not migrating. Note that TPH concentrations used to indicate potentially mobile product for soil in the vadose zone should not be used for impacted soil at the capillary fringe or in the saturated zone, because the water content in the soil pore spaces is higher.

The petroleum that remains as measurable product, sheen, or residual in the soil must have a low enough effective solubility so that it is not acting as a significant source to groundwater. For most sites, stable or declining concentrations of dissolved constituents in groundwater indicate that the petroleum is no longer acting as a significant source.

## 2. The site has been adequately characterized.

This includes adequate lateral and vertical delineation of petroleum in the subsurface (soil, groundwater, and soil vapor [if necessary]), and the identification and assessment of horizontal or vertical conduits that could intersect the plume and act as a preferential pathway for migration.

## 3. The dissolved plume is stable and is not migrating.

Chemical concentrations that do not increase or are stable over time are good indicators of a stable plume. Stable or decreasing plumes often display short-term variability in groundwater concentrations. This variability can be due to changes in (a) groundwater flow direction, (b) water level elevations, (c) purging and sampling procedures, (d) analytical procedures, (e) laboratories, and (f) other factors. These changes in concentration should not necessarily be interpreted as evidence of an unstable plume. Evaluating data over one hydrologic cycle is usually typical to determine plume stability. However, if seasonal changes in water levels and gradient direction are minor, then a full cycle may not be necessary; if seasonal changes are significant, then one cycle may not be adequate.

## 4. No water supply wells, deeper drinking water aquifers, surface water or other receptors are likely to be impacted.

If the plume is stable and not migrating (factor 3) then by definition it will not grow longer than its current extent. Therefore, if these receptors are outside the current plume extent, then they are unlikely to be impacted by the dissolved plume.

## 5. Beneficial use of the impacted groundwater will be restored within a reasonable time frame.

This factor involves documenting that there are no current uses of the impacted groundwater, and no anticipated future uses of the impacted groundwater within the time frame expected to be needed to meet WQOs. This information can be obtained from State or local agencies who are responsible for planning for future local water supply. An assessment of the length of time before WQOs will be met can be performed using trends in site-specific monitoring data; this can be a simple trend analysis.

Regarding the time frame for restoration of impacted groundwater, the SWRCB passed Resolution 2009-0081 which clarified that allowing for a reasonable time frame for impacted groundwater to reach WQOs, even if that time frame was lengthy, was consistent with existing SWRCB Resolutions and Policies (including Resolution 1992-0049). Depending on site-specific conditions, decades to centuries may be a reasonable time frame to reach WQOs because of the unlikelihood that the impacted groundwater will be used. The protective nature of existing well-construction practices, which include state and local requirements for depths of the sanitary well seals, should also be considered when evaluating the likelihood of COCs impacting the future uses of groundwater.

## 6. The groundwater plume does not pose a risk to human health or safety.

This factor considers potential risk from impacted groundwater, primarily via the vapor intrusion pathway; it does not assume that the impacted groundwater is ingested as drinking water.

Many groundwater plumes that meet these factors have been recognized as not posing a significant threat to human health, safety, and the environment, and natural attenuation has been relied upon to (1) protect unimpacted groundwater, (2) protect sensitive receptors such as supply wells and surface water, and (3) restore the beneficial use of impacted groundwater within a reasonable time frame.

## Other (Non-Risk-Based) Considerations

In addition to evaluating the exposure pathways for risk potential, there are some additional criteria that need to be met. These include making sure that product is not mobile and making sure that odor thresholds are not exceeded.

### Product Mobility

If the soil at the site is impacted and the screening levels for surface soil are to be used, or the site meets criteria of the LUFT-Specific Risk Screening, then the soil concentrations must also be below the point at which the product may move under gravity as a liquid phase (mobile product). The factors that control product mobility and migration and the concept of residual saturation were discussed in the [Fate and Transport](#) chapter. Soil-screening concentrations that reflect **residual saturation**, and therefore are the upper-limit concentrations before product in the vadose-zone soil would potentially be mobile as a bulk liquid, are provided below. These values are based on measured values in the literature for residual saturation of unweathered gasoline and diesel in various soil types (from Brost and DeVaul 2000), and are presented as

total petroleum hydrocarbons [TPH] concentrations. Table 12 shows the mobility limits for gasoline and diesel for four different soil types.

**Table 12. Mobility Limits (Maximum TPH Concentrations) for Fresh Gasoline and Diesel**

Soil Type	Gasoline mg/kg	Diesel mg/kg
Silt to fine sand	10,000	22,857
Fine to medium sand	5,833	13,333
Medium to coarse sand	3,387	7,742
Coarse sand and gravel	1,697	3,879
Coarse gravel	1,000	2,286

**Reference:** Brost and DeVaul (2000)

Note: these are the lowest concentrations presented in Brost and DeVaul for each soil type.

### Nuisance Odors

Some sites may have residual petroleum in near-surface soil (0 to 3 feet bgs) where **odors are evident** but human health risk posed by the petroleum is low. In these cases, aesthetic issues can be addressed by excavation, capping, vapor barriers, or other appropriate mechanisms.

### Limitations of the LUFT Risk Screening Tools

These screening tools can only be used at sites where adequate sampling and analysis have been completed to yield an accurate understanding of subsurface conditions. It is important to understand the underlying assumptions used in developing the screening tools in order to verify that the conditions at the site are consistent with the assumptions made. For example, if the LUFT screening levels assume that the soil source size is 45 feet × 45 feet and 6 feet thick, but the source at the LUFT site exceeds that size, then the screening tool should not be used and the exposure pathway may need to be evaluated using another method.

### Site-Specific Risk Assessment

If site COC concentrations exceed LUFT screening levels or have exposure pathways that are not screened out using the LUFT Risk Screening Tools, then a site-specific risk assessment may need to be performed. All risk assessments should be conducted according to existing technically defensible guidance. The site-specific risk assessment should be prepared by individuals who have significant expertise and experience in conducting this type of evaluation. All assumptions and parameters used in the analysis must be adequately documented (transparency) and all risk assessments must provide sufficient detail so that results may be duplicated/checked by others.

A few options for site-specific risk assessment include:

- Using a fate-and-transport model to evaluate the potential migration and attenuation of the chemicals using site specific calibration data when available.
- Using site-specific mass fraction information about the quantity of each chemical present in the TPH (especially valuable at weathered releases or releases other than gasoline or diesel).
- Considering the time until the site will be closed and accounting for source depletion during that time frame.
- Considering future uses of the site other than residential or commercial/industrial (e.g., parks, open space).

### Risk Management Decisions

Once the risk characterization is completed for an individual site, the focus turns to risk management. At this point, the risk manager considers the risk assessment results (including exposure assumptions and uncertainties) along with other technical, legal, economic, and social considerations to reach a regulatory decision as to the appropriate actions to be taken at the site. Factors that may be important in evaluating potential actions include efficiency, timeliness, equity,



administrative simplicity, consistency, public acceptability, technological feasibility, data quality, degree of certainty in future land use and groundwater use, and nature of the legislative mandate.

Risk management decisions for LUFT sites will be made on a case-by-case basis, consistent with Cal/EPA and EPA policy and guidance. The decision should take into account both site-specific and chemical-specific data, and multiple lines of evidence should be used to decrease the uncertainty in evaluating individual sites, as appropriate. Table 13 summarizes the basic decision logic and recommended management decisions to be considered in evaluating risk assessment results at a LUFT site. The target risks selected and the suggested actions are consistent with Cal/EPA and EPA (National Contingency Plan) recommendations for other types of sites.

**Table 13 - LUFT Risk Management Response Options**

Estimated Risk/Hazard	Response	Action(s)
Risk $\leq 1 \times 10^{-6}$ Hazard Index $\leq 1$	None	No further action
$1 \times 10^{-6} < \text{Risk} \leq 1 \times 10^{-4}$ Hazard Index $> 1$	Risk Management Decision	-Monitoring -Possible Mitigation -Possible Source Remediation -Possible Site Closure
Risk $> 1 \times 10^{-4}$ Hazard Index $> 1$	Mitigation Source Remediation Land Use Covenants Capping Site	-Appropriate risk mitigation -Source Remediation -Isolation of contaminants of concern from public and environment.

In addition to the specific guidance for evaluating risk assessment results, applicable statutory limits may also need to be considered in evaluating particular actions to be applied at any particular site. For example, for groundwater that is currently used as drinking water, California MCLs may need to be considered as appropriate cleanup levels. For groundwater that is not a potential source of drinking water during the time frame which it is anticipated that concentrations of COCs could exceed applicable water-quality criteria, again as documented in the site CSM, alternate risk management targets should be considered. In the case of recharge/discharge to surface water(s), risk management targets designed to protect aquatic life will need to be evaluated.

### **Risk Management and Corrective Action**

When risk evaluation results indicate that potentially significant health risks may be associated with the LUFT site, corrective action may be necessary to mitigate short- and/or long-term exposure. The [Remediation](#) chapter discusses some of the various corrective actions that may be effective at reducing the risk associated with a LUFT site.

### **References**

- Brost, J.B. and G.E. DeVaul. 2000. Non-Aqueous Phase Liquid Mobility Limits in Soil, Soils and Groundwater Research Bulletin No. 9., American Petroleum Institute (API), Washington, DC., June.
- Interstate Technology & Regulatory Council (ITRC). 2005. Examination of Risk-Based Screening Values and Approaches of Selected States. RISK-1. Washington, D.C.: Interstate Technology & Regulatory Council, Risk Assessment Resources Team. <http://www.itrcweb.org>
- ITRC. 2008. Use of Risk Assessment in Management of Contaminated Sites. RISK-2. Washington, D.C.: Interstate Technology & Regulatory Council, Risk Assessment Resources Team. <http://www.itrcweb.org>.
- Office of Environmental Health Hazard Assessment (OEHHA). 2005. Use of California Human Health Screening Levels in Evaluation of Contaminated Properties. Prepared by the California Environmental Protection Agency (Cal/EPA).
- Potter, T.L. and K.E. Simmons, 1998. Composition of Petroleum Mixtures. Volume 2 of the Total Petroleum Hydrocarbons Criteria Working Group Series. Amherst Scientific Publishers, Amherst MA. ISBN 1-884-940-19-6.
- Regional Water Quality Control Board (RWQCB) Region 2 – San Francisco. 2008. *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater*. Interim Final. May
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# Remediation

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## Scope of This Chapter

This chapter presents various approaches to remediation applicable to LUFT sites.

If the Conceptual Site Model (CSM) for a LUFT site indicates that there is a risk to human health, safety, and/or the environment, remedial action may be required.

This chapter provides an overview of several common remedial actions that may be employed at LUFT sites, but is not intended to include all available approaches.

When selecting a remedial approach it is important to evaluate and propose an appropriate remedial action that is technically feasible, specific to site conditions, and economically viable. An appropriate remedial action is any action that helps reduce or manage risk to an acceptable level. The selection of remedial action(s) should be made after developing an adequate CSM, assessing risks, developing closure goals/remediation objectives, and evaluating all options of remediation.

Remediation involves the breaking of the source-pathway-receptor linkage via:

- 1) Source Cleanup
- 2) Receptor Protection
- 3) Pathway Containment/Elimination
  - **Source Cleanup:** Reduction or elimination of risks by reducing the mass of the source and/or by changing its chemical composition to reduce its mobility or toxicity. Some commonly used technologies are excavation, soil-vapor extraction (SVE), air sparging, biosparging, dual-phase extraction, chemical oxidation, solidification/ stabilization, etc.
  - **Receptor Protection:** Reduction or elimination of risks by managing the exposure to the receptor. Examples include relocation of the receptor or providing an alternate water source where the current water source is contaminated. For sites that do not currently have a receptor, but which could pose a risk if a receptor were introduced, well-implemented institutional controls (e.g., restrictions on land use) can be employed to manage future potential risks.
  - **Pathway Containment/Elimination:** These are barriers (engineering controls) preventing migration of COCs from a source. This is different from source cleanup, because the barriers have little effect on the rate of source depletion and are control measures that will need to remain in place with appropriate institutional controls (ICs) until the source concentrations naturally decrease to acceptable levels or the receptor conditions change. Examples of pathway containment include: hydraulic capture by pump and treat, installation of low-permeability or permeable reactive barrier walls, sub-slab depressurization systems, etc. Engineering controls for vapor intrusion are discussed in [Appendix C](#).

Remedial actions are employed in either the unsaturated or saturated zones. Depending on where the CSM indicates the contamination to be present and the phase of contamination, the following remedial actions may be utilized and are discussed in further detail in this chapter.

### Unsaturated Zone Remediation:

- Soil Excavation
- Soil-Vapor Extraction
- Bioventing

### Saturated Zone Remediation:

- Air and Bio-Sparging
- *In-Situ* Groundwater Ozone Sparging
- *In-Situ* Groundwater Bioremediation
- Other Groundwater Remediation Technologies: Pump-and-Treat and Dual-Phase Extraction
- Natural Attenuation

As defined in the California Code of Regulations (CCR) Title 23 (Waters), Division 3, Chapter 16, Underground Tank Regulations Article 11 §2725, the responsible party (RP) shall propose a Corrective Action Plan (CAP) based on the information obtained during the site investigation and with concurrence from regulatory agencies. Details regarding the development of a CAP are discussed in the [CAP](#) chapter of this Manual.

Table 14 below presents a summary of LUFT remedial actions and the appropriate conditions for their use and subsequent sections provide an overview of the remedial actions.

Table 14 – Possible Remedial Actions at LUFT Sites

Contaminated Zone	Remedial Technology	When to Use	Cost
<b>Unsaturated (Vadose) Zone</b>	Soil Excavation	<ul style="list-style-type: none"> <li>• Rapid, definitive remediation</li> <li>• Limited contaminated area</li> <li>• Shallow and soil-only contamination</li> <li>• Heavy clay soils (&lt;3–5% sand or silt) which are unresponsive to other remediation technologies</li> </ul>	Low to High, depending on site conditions
	Soil-Vapor Extraction (SVE)	<ul style="list-style-type: none"> <li>• Contaminants are volatile</li> <li>• Contamination above groundwater table, with groundwater table &gt; 3 feet below ground surface (bgs)</li> <li>• Soils have high permeability, moderate moisture content, and low organic content</li> <li>• May be used near a building to prevent vapor migration into the building</li> </ul>	Moderate
	Bioventing	<ul style="list-style-type: none"> <li>• Soils have high permeability and moderate moisture content</li> <li>• Groundwater present at depth &gt; 3 feet bgs</li> <li>• Contaminants are aerobically biodegradable</li> <li>• Sites contaminated with mid-weight petroleum products</li> <li>• Site is away from basements, sewers, or other subsurface confined spaces</li> </ul>	Moderate
<b>Saturated Zone</b>	Air Sparging	<ul style="list-style-type: none"> <li>• Contaminants are volatile</li> <li>• Soils have moderate to high permeability</li> <li>• Contaminants are dissolved in groundwater and no free product is present</li> <li>• Site is away from basements, sewers, or other subsurface confined spaces</li> <li>• Contaminated groundwater is located in a confined aquifer</li> </ul>	Moderate
	Biosparging	<ul style="list-style-type: none"> <li>• Soils have high permeability</li> <li>• Contaminants are aerobically biodegradable</li> <li>• Contaminants are soluble and present mostly in groundwater</li> <li>• Site is away from basements, sewers, or other subsurface confined spaces</li> </ul>	Moderate
	<i>In-situ</i> Oxidation: Ozone Sparging	<ul style="list-style-type: none"> <li>• Soils have moderate to high permeability</li> <li>• Contaminants can be oxidized by ozone</li> <li>• Good application for contamination in shallow groundwater</li> <li>• Measures taken to avoid ozone reacting with nearby tanks or other underground utilities/lines</li> <li>• Potential for toxic by-product generation, such as hexavalent Cr(VI), must be evaluated</li> </ul>	Moderate
	<i>In-situ</i> Groundwater Bioremediation	<ul style="list-style-type: none"> <li>• Soils have moderate to high permeability</li> <li>• Contaminants are biodegradable</li> <li>• Contaminants are soluble and present mostly in groundwater</li> </ul>	Moderate
	Pump-and-Treat	<ul style="list-style-type: none"> <li>• Remediation is not time-critical</li> <li>• Contaminants are soluble and present mostly in groundwater</li> <li>• Adsorption of contaminants to soil is low</li> <li>• Can be used to create hydraulic barrier</li> </ul>	High
	Dual-Phase Extraction*	<ul style="list-style-type: none"> <li>• Sites with clayey/silty soil where groundwater flow rates are low</li> <li>• Contaminants present in soils below the water table.</li> </ul>	High
	Natural Attenuation*	<ul style="list-style-type: none"> <li>• Remediation is not time-critical</li> <li>• Site must be evaluated for natural attenuation potential; approval from agencies is required</li> <li>• Subsurface conditions will not be disturbed during attenuation period</li> </ul>	Moderate

\* Applicable when contamination is present in both the saturated and unsaturated zones.

# Remediation

## LNAPL

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UST 40 CFR 280.64 (1988) states that “free product” (light-non-aqueous-phase liquid, or LNAPL) should be removed “to the maximum extent practicable as determined by the implementing agency.” However, metrics or endpoints to define the “extent practicable” have not been clearly defined, and many agencies use LNAPL thickness in a groundwater well as a metric for remediation. This is inaccurate, because the thickness of LNAPL in a groundwater well may not correlate with the amount of LNAPL in the formation, due to the physico-chemical properties of LNAPL as discussed in the [Fate and Transport](#) chapter. For example:

- LNAPL does not float on the water table in a uniform, high-saturation, “pancake”-like layer.
- LNAPL is distributed above, at, and below the water table at saturations that vary vertically.
- Seasonal water-table fluctuations can continually change the extent of the unsaturated and saturated zones, causing the LNAPL to redistribute vertically (also creating a “smear zone” of entrained LNAPL in the soil column). Consequently, the amount of mobile LNAPL changes, but the total LNAPL volume is unchanged. The starting volume of LNAPL, as well as can be determined, is the volume of gasoline lost from the fueling source.
- LNAPL is mobile when LNAPL saturation is greater than the residual saturation.
- Migration of LNAPL cannot occur unless LNAPL is present within the mobile range of LNAPL saturations.
- Not all mobile LNAPL necessarily migrates, but LNAPL must be mobile in order to migrate (ITRC 2009).
- In the formation, LNAPL may be under confining pressure and its true thickness may differ as compared with the apparent thickness present in a monitoring well which is not under confining pressure. In fact, the well may act as a collection point for LNAPL due to the pressure differential between the formation and ambient air (which is the baseline condition within most monitoring wells).

Based on an understanding of how LNAPL reacts in the subsurface, it is important to set realistic LNAPL remedial objective(s) and metrics and select the appropriate LNAPL remedial technology(ies) to achieve the objectives, all of which must be consistent with the CSM. It is also important to realize that, even under ideal conditions, only a portion of the total volume of the LNAPL release will be recoverable and some portion of the LNAPL mass will remain in the subsurface as immobile residue.

### LNAPL Remediation Approaches

LNAPL is remediated by recovering mass, controlling mass, or by implementing a LNAPL phase change (ITRC 2009). It may be necessary to implement a combination of the LNAPL remedial actions to achieve remedial objectives. The following subsections are excerpted from the December 2009 ITRC document entitled *Evaluating LNAPL Remedial Technologies for Achieving Project Goals* and summarize LNAPL remediation approaches and performance metrics.

#### LNAPL Mass-Recovery Technology

LNAPL mass-recovery technologies directly recover LNAPL via physical removal and are the most frequently used technologies for LNAPL remediation. Examples of mass-recovery technologies include excavation or hydraulic recovery (e.g., LNAPL pumping or skimming, or dual-phase extraction) or technologies such as absorbent materials which are changed out periodically, etc. Hydraulic recovery may be pursued with or without flow augmentation by using remedial techniques that reduce LNAPL viscosity or interfacial tension (e.g., surfactants or solvents), thereby enhancing LNAPL flow.

LNAPL mass-recovery technologies address saturation-reduction-based LNAPL remedial objectives, which can be a key objective for a migrating plume. With the exception of excavation, which can achieve LNAPL removal (subject to logistical and practical limits), LNAPL mass recovery using pumping or skimming technologies is limited to reducing LNAPL saturation to residual saturation. At residual saturation, LNAPL will not flow and, therefore, hydraulic recovery is no longer possible.

### LNAPL Phase-Change Technology

LNAPL phase-change technologies do not directly remove LNAPL from the environment as is the case for LNAPL mass-recovery technologies. Instead, LNAPL phase-change technologies exploit the tendencies of LNAPLs to partition to other phases by increasing the rates of volatilization or dissolution of the LNAPL constituents by different means. Those LNAPL constituents are degraded or captured in the vapor or dissolved phase and removed from the environment. As the LNAPL constituents are removed from the LNAPL, its composition is changed by loss of those constituents that readily degrade, volatilize, or dissolve.

Examples of remediation technologies that implement LNAPL phase changes include soil-vapor extraction. LNAPL phase-change technologies are primarily applicable to composition change-based LNAPL remedial objectives, which can be a key objective where groundwater and vapor concentrations are also to be reduced. With LNAPL phase change comes some saturation reduction. These technologies may therefore have some secondary application for saturation-based LNAPL remedial objectives.

LNAPL phase-change technologies are not limited by residual LNAPL saturation because they do not depend on the presence of mobile LNAPL. Some LNAPL phase-change technologies are more elaborate to design and implement than LNAPL mass-recovery technologies, and their costs and limits may not be as well understood as those of LNAPL mass-recovery technologies. Thus, LNAPL phase-change technologies may be more costly to design and deploy, but strategic/targeted application may minimize such limitations and possibly shorten the overall LNAPL remediation life cycle. For example, to achieve a remedial objective of LNAPL recovery to saturations less than residual, it might be more appropriate to deploy the LNAPL phase-change remedial technology after the LNAPL mass-recovery technology has reached its recovery limit or an LNAPL remediation goal is reached that is set to transition between the two technologies.

### LNAPL Mass-Control Technology

LNAPL mass-control technologies stabilize migrating LNAPL by reducing the LNAPL saturation via blending a binding agent with the LNAPL zone (mixing technologies) or by physically blocking LNAPL migration (containment technologies). Such technologies alone may satisfactorily meet the remedial objective or can be used in combination with LNAPL mass-recovery and/or LNAPL phase-change technologies. Additional long-term operation and maintenance and stewardship requirements may also be warranted, depending on site conditions and property use. Specifically, LNAPL mass-control technologies are primarily suited for saturation-based LNAPL remedial objectives by limiting mobility or eliminating migration. The containment technologies are limited in applicability to LNAPL saturations in excess of residual saturation, since at residual saturations the LNAPL body is, by definition, immobile. In some instances, mixing technologies may also reduce cross-media impacts (e.g., recharge infiltration and leaching through the LNAPL zone) since some binding agents (e.g., Portland cement) can reduce the soil permeability of the LNAPL zone or degrade the volatile or soluble LNAPL constituents.

### LNAPL Remedial Performance Metrics

For each LNAPL remediation goal, one or more “performance metrics” are defined. Performance metrics are measurable characteristics that relate to the remedial progress of a technology in abating the concern. The different LNAPL remediation technologies function differently and, therefore, the performance metrics used to demonstrate progress toward and achievement of the LNAPL remediation goal depend on the technology used. Ideally, each performance metric has a predetermined value that describes when the technology has reached the limits of beneficial application. That is the end-point metric for the technology chosen. Table 15 lists example performance metrics for hypothetical LNAPL remediation goals.



Table 15– Example LNAPL Remediation Performance Metrics

Example Performance Metrics	Description/Comments
LNAPL transmissivity	Hydraulic recovery is likely ineffective for plumes exhibiting low LNAPL transmissivity.
LNAPL/water recovery ratio	Ratio of unit volume of LNAPL recovered per unit volume of water. Decreasing ratio indicates decreasing recovery effectiveness.
LNAPL/vapor recovery ratio	Ratio of unit volume of LNAPL recovered per unit volume of vapor. Decreasing ratio indicates decreasing recovery effectiveness.
Limited/infrequent in-well LNAPL thickness	Stated LNAPL thickness goal or LNAPL thickness typically not observed in monitoring well under average site conditions. Indicative that LNAPL is not consistently recoverable and the majority of remaining impacts are residual; excavation may be the only feasible option.
Decline-curve analysis	Analysis of unit volume of LNAPL recovery or recovery rate per unit time. Declining curve indicates decreasing recovery effectiveness (e.g., decline-curve analysis indicates that, based on the LNAPL recovered, the remaining LNAPL is either small or the time to recover relative to the remaining volume may be impractical).
Unit cost per gallon LNAPL recovered	Increasing cost/gallon of LNAPL recovered indicates decreasing cost effectiveness (cost may not always be in line with regulatory rules)
Soil concentration/soil concentration profile	Soil concentrations in LNAPL area meet regulatory criteria, or desired soil concentration profile demonstrated.
LNAPL recovery rate vs. estimated LNAPL flux	The recovery system either diminishes the driving LNAPL gradient and/or achieves a higher recovery rate than estimated by flux migration across the width of the LNAPL body front.
LNAPL saturation profile	Comparison of saturations before and after treatment to demonstrate reduced saturations.
LNAPL body footprint stabilized	Will technology counter existing LNAPL driving gradient and/or capture migrating LNAPL? Comparison of LNAPL plume footprint before and after treatment to demonstrate non-increasing footprint size.
Dissolved-phase plume stabilized	If exhibited, then it is an indication of a stable LNAPL body.
No first LNAPL occurrence in down-gradient well	LNAPL never enters a monitoring well installed outside of LNAPL body.
Soil concentration for soil stability	Concentrations reduced to the regulatory limit.
Soil concentrations	Concentrations reduced to the regulatory limit.
Dissolved-phase concentration	Concentrations reduced to regulatory standard at a compliance point.
LNAPL composition	Reduced mole fraction of volatile or soluble LNAPL constituents.
Vapor-phase concentration	Concentrations reduced to regulatory standard at a compliance point.

Source: ITRC – Evaluating LNAPL Remedial Technologies for Achieving Project Goals, December 2009

# Remediation in the Unsaturated Zone:

## Soil Excavation



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Soil excavation is the removal of contaminated soil using heavy machinery such as backhoes. The excavated soil is either disposed of at a landfill or land-farmed. Land-farming involves spreading excavated contaminated soils in a thin layer on the ground surface and stimulating aerobic microbial activity within the soils through aeration and/or the addition of minerals, nutrients, and moisture.

### Advantages of Soil Excavation

- Proven performance; readily available equipment.
- Can achieve significant concentration reduction.
- Short treatment times with quick turn-around, particularly when there are immediate risks to human health, safety, and the environment.
- Can be applied at sites with free product (Non-Aqueous Phase Liquid [NAPL]), can be combined with other technologies.
- Under appropriate conditions, soil may be re-used.

### Disadvantages of Soil Excavation

- Significant disturbance to site operations.
- May be costly due to disposal costs.
- Not applicable in water-bearing zone.

### Application

Remedial soil excavation is effective at removing the majority of impacted soil associated with a petroleum release at a LUFT site, but can be more invasive and can present more challenges than *in-situ* measures for the following reasons:

- Most gas station site soils deeper than 20 to 50 feet bgs are not easily removable without shoring due to limited space.
- Excavation of soils within the water-bearing zone is logistically challenging and more costly than removing dry soil.
- Excavation requires an area free of surface buildings and subsurface structures.
- Excavation and transportation of excavated soil involve heavy truck traffic and create noise, dust, and often odors and vibrations that may impact the community.
- Excavation may be less cost-effective than many forms of *in-situ* remediation, and may therefore not be reimbursable by the UST Cleanup Fund if a similarly effective, lower-cost remediation method is available.

Under some circumstances, however, remedial excavation is the best remediation method available. Conditions which may indicate that excavation is an appropriate remedial technology include:

- Property-related issues, such as redevelopment, which may require rapid, definitive remediation measures.
- Limiting excavation to certain site areas, such as the immediate UST area, to expedite and reinforce other forms of remediation.
- Shallow, soil-only plumes with limited lateral and vertical extent.
- Heavy clay soils (<3–5% sand or silt) which are unresponsive to other forms of remediation (within 2 to 25 feet of grade). Deeper clayey soils may require other *in-situ* remediation methods, such as bioremediation, fracturing, heat treatment, etc.

### Limits of Excavation

When planning excavation projects, it is most cost-effective to establish the limits of excavation in advance of mobilization and field efforts. There is no one scientific method approved for statewide use in California to calculate site-specific

excavation cleanup goals, and there is also a high degree of variability among regulatory agencies regarding practicable limits. The lead agency should be consulted regarding site-specific cleanup goals.

## Soil Remediation Verification

According to CCR Title 23, Division 3, Chapter 16, Article 11 §2725, verification monitoring is required to evaluate the effectiveness of the corrective action.

For remedial excavations, soil samples are collected after the contaminated soil has been removed to verify the effectiveness of the removal. One example of soil verification testing is the advancing of one or two soil borings in the former areas of highest concentrations, advanced vertically to the total depth of the plume.

Verification soil sample depths coincide with those which formerly exhibited the highest concentrations and/or in areas of lithologic interest, such as the capillary fringe. It is advisable to check with the lead regulatory agency prior to conducting such work, because a soil verification sampling work plan may be required if verification soil samples were not conceptually outlined as part of the CAP.

Once post-remediation soil analytical data are available, the information is submitted to the regulatory case worker for comparison with pre-remediation levels to determine the next steps. If post-remediation soil concentrations are at or below levels previously established by the agency for No Further Action, the agency can be requested to approve no further soil remediation. Agency approval is required.

If, however, soil concentrations have *not* been sufficiently reduced, and the remediation system or process used has reached its performance capacity limits, the agency may require a re-evaluation of remedial options and selection of a different remedial solution.

# Remediation in the Unsaturated Zone:

## Soil-Vapor Extraction



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Soil-vapor extraction (SVE), also known as “soil venting” or “vacuum extraction,” is an *in-situ* remediation technology that reduces concentrations of volatile petroleum-hydrocarbon constituents adsorbed to soils in the unsaturated (vadose) zone (EPA 1994).

In this technology, a vacuum is applied to the soil matrix via wells. The reduced pressure due to the vacuum causes these volatile constituents to transform into the vapor phase and move toward the extraction points (i.e., wells). The extracted vapors are then treated as necessary (commonly via carbon adsorption) before being released harmlessly to the atmosphere. The increased air flow through the subsurface can also stimulate biodegradation of some contaminants, especially those that are less volatile.

**Drilling Down.** The introduction of air into the soil can stimulate indigenous soil bacteria to grow due to the introduction of oxygen, with the result that the bacteria consume substantial quantities of remaining hydrocarbons. The presence of carbon dioxide in the extracted soil vapors is an indicator of bacterial activity. As it normally takes 6 months or more to establish such synergistic bacterial colonies, vapor extraction processes of shorter duration won’t likely show this side effect, or there may be a delay in seeing evidence of colony growth.

Wells may be either vertical or horizontal, although horizontal extraction wells are much more costly than multiple vertical wells and are generally not used at LUFT sites. In areas of high groundwater levels, water-table depression pumps may be required to offset the effect of upwelling induced by the vacuum. One of the best ways to avoid upwelling during SVE is to reduce the applied vacuum.

### Advantages of SVE

- Proven performance; readily available equipment; easy installation.
- Minimal disturbance to site operations.
- Shorter treatment times (usually 6 months to 2 years under optimal conditions).
- Cost competitive: \$20–\$50/ton of contaminated soil.
- Can be applied at sites with free product (NAPL) and can be combined with other technologies.

### Disadvantages of SVE

- Due to residual petroleum saturation concentrations reductions greater than 90% of the initial finding are difficult to achieve.
- Effectiveness is less certain when applied to sites with low-permeability soil or stratified soils.
- May require costly treatment for atmospheric discharge of extracted vapors.
- Air-emission permits are generally required.
- SVE treats only unsaturated-zone soils; other methods may also be needed to treat saturated-zone soils and groundwater.

### Application

SVE has been proven effective in reducing concentrations of volatile organic compounds (VOCs) and certain semi-volatile organic compounds (SVOCs) found in petroleum at UST sites. SVE is generally more successful when applied to the lighter (more volatile) petroleum products such as gasoline. Diesel fuel, heating oils, and kerosene, which are less volatile than gasoline, are not readily removed by SVE, nor are lubricating oils, which are non-volatile.

**Important!** SVE is generally not effective in treating soils below the top of the capillary fringe unless water-table depression pumps are used to draw down the water table. SVE is also generally inappropriate for sites with a groundwater table less than 3 feet bgs. Special considerations must be taken into account for sites with a groundwater table less than 10 feet bgs, because groundwater upwelling can occur within SVE wells under vacuum pressures, potentially occluding well screens and reducing or eliminating vacuum-induced soil vapor flow.

SVE may be appropriate near a building foundation to prevent vapor migration into the building. In this case, the primary goal may be to control vapor migration and not necessarily to remediate soil.

## Operating Principles

In SVE, a vacuum is applied to the contaminated soil matrix through extraction wells. This creates a negative pressure gradient, which in turn causes movement of vapors toward these wells. Volatile constituents in the vapor phase are readily removed from the subsurface through the extraction wells. The extracted vapors are then treated (as necessary) and either discharged to the atmosphere or possibly re-injected to the subsurface (if permitted by applicable state laws).

Some of the factors that determine the effectiveness of SVE are:

- Permeability of the soil
- Soil structure and stratification
- Soil moisture content and soil organic content
- Depth to groundwater
- Annual precipitation

The permeability of the soil affects the rate of air and vapor movement through the soil: the higher the permeability of the soil, the faster the movement and (ideally) the greater the volume of vapors available for extraction.

Soil structure and stratification are important to SVE effectiveness, because they can affect how and where soil vapors will flow within the soil matrix under extraction conditions. Therefore it is important to detail subsurface geology with continuous information to determine structural characteristics (e.g., layering, fractures) can result in preferential flow behavior that may lead to ineffective or significantly extended remediation times if these structures are positioned so that the induced air flow does not pass through the area of contamination.

High moisture content in soils can reduce soil permeability and therefore the effectiveness of SVE by restricting the flow of air through soil pores. Fine-grained soils create a thicker capillary fringe (increasing moisture content in the soil) than do coarse-grained soils. However, soils which are too dry (moisture content too low) will result in reduced removal rates. In addition, soils with high organic content, similar to too-dry soils, will also have a reduced VOC removal rate.

**Definition.** **Capillary Fringe** is defined as the area above the water table where water seeps up into the soil via capillary action. The height of the capillary fringe varies with soil porosity and type.

## System Design

Design radius of influence (ROI) is the most important parameter to be considered in the design of an SVE system. The ROI is defined as the greatest distance from an extraction well at which a sufficient vacuum and vapor flow can be induced to adequately enhance volatilization and extraction of contaminants from the soil. Extraction wells should be placed so that the overlap in their ROIs completely covers the area of contamination.

Fluctuations in the groundwater table should also be considered when designing an SVE system. Significant seasonal or daily (tidal or precipitation-related) fluctuations may, at times, submerge some of the contaminated soil or a portion of the extraction well screen, making it unavailable for air flow. This is most important for horizontal extraction wells, where the screen is parallel to the water-table surface.

Surface seals should be included in an SVE system design to prevent surface-water infiltration. They can reduce air-flow rates, reduce emissions of fugitive vapors, prevent vertical short-circuiting of air flow, and/or increase the design ROI. These results are achieved because surface seals force fresh air to be drawn from a greater distance from the extraction well.

When surface seals are used, the lower pressure gradients result in decreased flow velocities. These decreased flow velocities may require a higher vacuum to be applied to the extraction wells.

## Pilot Testing

Pilot studies are an important part of the design phase of a full-scale SVE system. They provide information on the concentration(s) of VOCs likely to be extracted during the early stages of operation of the SVE system and evaluate the effectiveness of an SVE design.

Pilot studies typically include short-term (1 to 30 days) extraction of soil vapors from a single extraction well, which may be an existing monitoring well at the site. Longer-term pilot studies (up to 6 months) which utilize more than one extraction well may be appropriate for sites with more widely spread contamination.

In some instances, it may be appropriate to evaluate the potential of SVE effectiveness using a screening model such as HyperVentilate (EPA 1993). HyperVentilate can be used to identify required site data, decide whether SVE is appropriate at a site, evaluate air permeability tests, and estimate the minimum number of wells needed. It is not intended to be a detailed, SVE-predictive modeling or design tool.

## Pilot Testing Considerations and Preparations

Well(s) to be used during the pilot test are installed in close proximity to the source area undergoing remediation. The well screen and filter pack are, in most cases, no longer than 10 feet to avoid friction loss. Wells are located in the vadose zone or capillary fringe, above the equilibrated groundwater level, to avoid pulling water over the screen (no vapor flow will occur under these circumstances). To maximize flow, extraction wells typically have a larger screen slot size and/or a sand filter particle size than those normally used for a groundwater monitoring well.

It may be appropriate to use a groundwater monitoring well for test purposes if it has a screen interval extending 5 feet or more above the top of the equilibrated water level.

To provide the most flexibility during the test, observation well(s) should be spaced between 10 and 20 feet from the extraction point. If wells are too far away, vacuum changes will not be observed. Most soil types exhibit extraction ROIs ranging from 5–10 feet (clays) to 40–50 feet (sands) at moderate extraction rates (100–250 cubic feet per minute [cfm]). If the test shows no response from wells at a distance of 10–20 feet from the extraction point, either there are construction problems with one or more wells, the test has been conducted incorrectly (for example, too much vacuum has been applied, resulting in upwelling water sealing off the extraction well screen), or the soil is too impermeable for vapor extraction to be an effective remediation measure.

Soils containing a high percentage of clay usually do not respond well to SVE, but any percentage of silts, sands, or gravels generally increases the ability of the soil to be vented. One extraction well and one to two observation wells are minimal requirements for short-term tests.

If soil types vary significantly laterally and/or vertically across the site, more extraction and/or observation wells may be needed to get an idea of potential vapor flow patterns.

Ideally, observation wells should be screened in at least part of the same depth interval as the extraction well(s), unless the soil types are more permeable (i.e., mostly sandy or gravelly), or if clay/silt lenses are laterally discontinuous (“pinch out”) between the areas where the injection and observation wells are located.

## Pilot Testing Procedure

Prior to test start-up, identify wells and equipment monitoring points. During the initial test start-up, record separate baseline vapor monitor concentrations, air flow rate, vacuum, temperature, humidity, screen interval, and depth-to-water measurements (field data) for each extraction and observation well. Influent air manifold and wellhead equipment should allow for concurrent reporting of isolated field data measurements from individual extraction wells.

Tighten piping, hose connections, and seals to prevent leaks. Vacuum is then applied to the extraction wells at two or three different levels, starting with the lowest possible applied vacuum. During the test, field data from the test wells are recorded at specified intervals proposed in the work plan. Monitoring can range from every 30 seconds to once every 30 minutes or more.

Samples may be collected into vapor sampling containers for laboratory analysis at periodic intervals in order to confirm that field sampling is accurate. These samples are generally collected less frequently than samples taken with field monitors (for example, once at the beginning, middle, and endpoint of the test).

Observation well pressure gauges are checked for changes throughout the test, usually before starting the test, and before and after changing the applied vacuum.

### Data Analysis and Interpretation

There are many mathematical models to determine the ROI based on laminar flow equations. Studies (DiGiulio 1992, EPA 2001) have identified a general rule of thumb that can be used for SVE system design purposes: 0.1 inch of water vacuum is the minimum level required to induce vapor flow. In practice, 0.2 inch of water vacuum is a more conservative value.

This means that if, during a test, an observation well does not show at least 0.1–0.2 inch of water response, and the applied vacuum is the highest that can be applied without drawing water over the extraction well screen, then the ROI is less than the distance between the extraction and the observation well(s).

### Remediation Application

At sites where soil types are not uniform (that is, they vary laterally and vertically), the ROI may be similarly variable. Ideally, the ROI in uniform formations translates to a circular area of influence when drawn on a plan-view site map. Non-uniform soils create non-circular areas of influence. In cross-section, the area of influence extends upward from the point of extraction in a cone shape.

Reviewing extraction test results while simultaneously viewing a cross-section can often help with interpretation. Clay soils may have an ROI of <5 feet to >10 feet, depending on the amount of silt or sand present. Silts tend to have an ROI of 15 to 25 feet, and sands can have an ROI of 40 feet or more. As soils dry due to repeated exposure to air, the ROI influence can change over time.

Spacing wells slightly closer together than the 0.1 inch of water vacuum response predicts may help prevent zones from forming between wells where the induced vacuum is too weak to create the desired remediation effect. Spacing wells too closely, however, can be inefficient and cost-ineffective.

Where different soil types exist, multiple source zones extending over large vertical distances may necessitate the installation of several extraction wells screened at varying vertical elevations. Well-screen slot size and filter pack should be designed to ensure optimal contaminant removal for specific soil types, because the vapor flow will follow the path of least resistance.

**For Example,** a vapor-extraction well that is screened across both sand and clay soils will remediate only the sand, leaving the clay largely as-is.

Wells to address different soil types can be installed as “clusters” (separate wells near each other) or as “nested” wells (differently constructed wells in the same borehole). Local agencies may have regulations restricting or preventing nested-well construction.

The seal on the top of the filter pack should be of sufficient thickness and installed so as to prevent leaks. Multiple source zones extending over large vertical distances and/or zones of low permeability may necessitate the installation of several extraction wells screened at varying vertical elevations.

During sustained extraction (full-scale implementation), sandy/gravelly soils will usually show high levels of vapor removal at first with relatively quick declines in concentrations due to low adsorptive capacity and the relatively high permeability of the soil. Silty/clayey soils have different grain structures and permeability characteristics, and usually show more gradual changes in extracted vapor concentrations over time.

### Vapor Treatment

Catalytic/thermal oxidizers are more cost-effective at higher extracted vapor levels (i.e., 3–5% or more of the Lower Explosive Limit [LEL]), while granular activated carbon systems are more cost-effective at lower extracted vapor levels (1–2% LEL). Oxidizers incinerate off-gas, while carbon systems adsorb vapors and must be replaced when saturated.



Sites with mixed soil types may require sequential pieces of equipment. For example, an oxidizer may be appropriate for several months after startup while sandy strata are being treated (high rates of vapor generation), followed by transition to carbon later in the remediation process to remediate silts and clays with lower off-gassing rates.

**Further Reading.** Variations and/or enhanced test procedures are available from a variety of sources, including EPA's *Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure*. EPA/600/R-01/070. September 2001.

## Rebound Testing

Rebound testing is used to determine whether the SVE system has reached its performance limit, and is normally conducted before collection of soil verification samples.

For soil remediation, stabilization of extracted vapor levels is verified by “pulsing” (turning the system on and off for a certain period of time) to check for “rebound” (increased concentrations after a period of system dormancy). If, after restarting, extracted vapor levels show concentrations at or near the levels observed before shutdown, the vapor-extraction process has reached its performance limit.

If concentrations return to levels at or near those observed early in the remediation process, then the system is usually re-started and operated for a brief period (for example, 1 to 4 weeks) and then shut down again for further rebound testing. If, after several such cycles, the concentrations fail to stabilize at levels close to those observed before the shutdown series began, additional evaluation of the remediation method or specific application (i.e., number and screening of extraction wells) may be appropriate. If the concentrations after the “off” cycle are near or less than the concentrations before the shutdown, the regulatory agency can be requested to evaluate removal of the remediation system.

Due to low rates of adsorption and because most of the hydrocarbon mass is removed during the advective stage, sandy soils usually show no to low rebound effects, while silty/clayey soils may require extensive pulsing to attain stable minimum levels. Clayey/silty soils often show rebound due to slower rates of desorption because of the dominance of diffusional processes in low-permeability soils.

The completion of groundwater extraction remediation is largely evidenced by declining concentrations of COCs in the groundwater plume. For groundwater extraction processes, “rebound” testing can consist of turning the system off over a period of months to see whether concentrations remain at stable, low levels, or if they increase.

General remediation rebound testing, where groundwater has been affected, consists of a pre-determined, post-remediation groundwater monitoring period. The regulatory agency determines this period, usually between 6 months and 1 year. Parameters to be analyzed during the post-remediation monitoring period usually are limited to primary COCs. An extended period of post-remedial monitoring may be required for sites in close proximity to receptors.

If post-remediation groundwater concentrations remain stable at or near those observed when remediation was halted for the duration of the post-remediation monitoring period, the agency can be requested to evaluate for closure. If groundwater concentrations “rebound” to levels near those at the start of remediation or to levels above approved closure goals during the post-remediation monitoring period, these data can be submitted to the agency with recommendations for the next required steps.

**Definition: Significant Rebound** is a relative term. If an SVE system started operations at 5,000 parts per million by volume [ppm(v)] and, prior to shutdown, extracted concentrations declined to 50 ppm(v), a “significant rebound” might be post-shutdown levels of 300 to 500 ppm(v). However, if pre-remediation groundwater concentrations were at a maximum of 13,000 micrograms per liter (µg/L) of MTBE, which declined to 300 µg/L MTBE and then “rebounded” to 400 µg/L MTBE, this might not be evidence of true rebound.

Rebound considerations are also dependent on site-specific factors, such as risk and receptor setting, pre- and post-remediation conditions, etc.

Based on verification testing completed to regulatory specification, if concentrations show declines below agency-approved closure goals, the agency will most likely close the case.

If, however, after application of the approved remedial process, concentrations have declined but are still above remediation goals due to limitations of the technology, application, or other factors, this Manual recommends contacting the lead regulatory agency for further guidance. If possible, alternate paths to closure will have been included in the CAP as contingency measures to facilitate their implementation, should the original remedial process prove insufficient to attain closure.

## Remediation Completion

Once extracted vapor concentrations have been stabilized, no additional change can be achieved, or the system has reached its performance limit, the general risk that remains needs to be assessed and a determination as to whether additional soil remediation is necessary made. Removal of the majority of the hydrocarbon plume in soil often sufficiently reduces the risk to groundwater and/or potential receptors such that no further remediation is necessary. Post-remediation soil concentrations can be evaluated by collecting soil samples in the former area of highest concentrations.

**Further Reading.** The text in this chapter is an excerpt from the publication by the Office of Underground Storage Tanks (OUST), “How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers” (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases. <http://www.epa.gov/swerust1/pubs/tums.htm>

# Remediation in the Unsaturated Zone:

## Bioventing

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Bioventing is an *in-situ* remediation technology that uses indigenous microorganisms to biodegrade organic constituents adsorbed onto soils in the unsaturated zone. Soils in the capillary fringe and the saturated zone are not affected. Through bioventing, the activity of indigenous bacteria is enhanced by inducing air (or oxygen) flow into the unsaturated zone (using extraction or injection wells) and, if necessary, by adding nutrients.

When extraction wells are used for bioventing, the process is similar to SVE. However, while SVE removes constituents primarily through volatilization, bioventing systems promote biodegradation of constituents and minimize volatilization (generally by using lower air-flow rates than SVE does). In practice, some degree of volatilization and biodegradation occurs when either SVE or bioventing is used.

### Advantages of Bioventing

- Uses readily available equipment; easy to install.
- Creates minimal disturbance to site operations. Can be used to address inaccessible areas (e.g., under buildings).
- Requires short treatment times: usually 6 months to 2 years under optimal conditions.
- Cost competitive: \$45–\$140/ton of contaminated soil.
- Easily combinable with other technologies (e.g., air sparging, groundwater extraction). May not require costly off-gas treatment.

### Disadvantages of Bioventing

- High constituent concentrations may initially be toxic to microorganisms.
- Not applicable to certain site conditions (e.g., low soil permeabilities, high clay content, insufficient delineation of subsurface conditions).
- Cannot always achieve very low cleanup standards.
- Permits generally required for nutrient injection wells (if used). (A few states also require permits for air injection.)
- Only treats unsaturated-zone soils; other methods may also be needed to treat saturated-zone soils and groundwater.

### Application

All aerobically biodegradable constituents can be treated by bioventing. In particular, bioventing has proven to be very effective in remediating releases of petroleum products including gasoline, jet fuels, kerosene, and diesel fuel. Petroleum products are generally biodegradable regardless of their molecular weight, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients.

**Tip:** Bioventing is most often used at sites with mid-weight petroleum products (e.g., diesel fuel and jet fuel), because lighter products (e.g., gasoline) tend to volatilize readily and can be removed more rapidly using SVE. Heavier, more stable products (e.g., lubricating oils) generally take longer to biodegrade than lighter products.

**Important!** Bioventing is not appropriate for sites with groundwater tables less than 3 feet bgs. Special considerations must be taken into account for sites with a groundwater table less than 10 feet bgs, because groundwater upwelling can occur within bioventing wells under vacuum pressures, potentially occluding screens and reducing or eliminating vacuum-induced soil-vapor flow. This potential problem is not encountered if injection wells, instead of extraction wells, are used to induce air flow.

## Operation Principles

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, protozoa, and actinomycetes. In well-aerated soils, which are most appropriate for bioventing, these organisms generally use oxygen to metabolize. Of these organisms, bacteria are the most numerous and active group, particularly at low oxygen levels. Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. Nutrients, including nitrogen and phosphorus, are also required for cell growth.

Hydrocarbon-degrading bacteria use oxygen to metabolize organic material and yield carbon dioxide and water in a process commonly referred to as *aerobic respiration*. The biodegradability (that is, the measure of a constituent's ability to be metabolized by these bacteria) of the constituents present will determine both the rate and the degree at which the constituents will be metabolized by microorganisms. To biodegrade large amounts of petroleum hydrocarbons, a substantial bacterial population is required, which in turn requires oxygen for both the metabolic process and the growth of the bacterial mass itself. Approximately 3 to 3.5 pounds of oxygen are needed to degrade 1 pound of petroleum product.

The permeability of petroleum-contaminated soils will determine the rate at which oxygen can be supplied to hydrocarbon-degrading microorganisms found in the subsurface. In general, the type of soil will determine its permeability. Fine-grained soils (e.g., clays and silts) have lower permeabilities than coarse-grained soils (e.g., sands and gravels). Note that the ability of a soil to transmit air, which is of prime importance to bioventing, is reduced by the presence of soil water, which can block the soil pores and reduce air flow. This is important to consider for fine-grained soils, which tend to retain water.

Soil structure and stratification are important to bioventing because they affect how and where soil vapors will flow within the soil matrix when extracted or injected. Structural characteristics such as micro-fracturing can result in higher permeabilities than expected for certain soils. Increased flow will occur in the fractured but not in the unfractured media (e.g., clay). Stratification of soils with different permeabilities can dramatically increase the lateral flow of soil vapors in more permeable strata, and at the same time reduce the soil-vapor flow through less-permeable strata. This preferential flow behavior can lead to ineffective or extended remediation times for less-permeable strata or to the possible spreading of contamination if injection wells are used.

**Note:** Bioventing differs from SVE in one fundamental way: the objective is to induce only sufficient air flow to enhance natural biodegradation of the contaminants, but not enough to cause them to volatilize. Air flow may be induced either by extracting soil vapor or injecting atmospheric air. Because of the lower air flow required to achieve bioventing, there is less likelihood than with SVE of causing contaminants to be forced into areas where they could potentially cause problems (e.g., vapor intrusion in basements). For extraction systems, there is usually less of a need for vapor treatment than for SVE systems.

## System Design

In general, remediation approaches that rely on biological processes should be subject to field pilot studies to verify and quantify the potential effectiveness of the approach and provide data necessary to design the system. For bioventing, these studies may range in scope and complexity from a simple soil column test or microbial count to field respirometry tests and SVE (or injection) pilot studies. The scope of pilot testing or laboratory studies should be commensurate with the size of the area to be remediated, the reduction in constituent concentration(s) required, and the results of the initial effectiveness screening.

Design ROI is an estimate of the maximum distance from a vapor-extraction (or injection) well at which sufficient air flow can be induced to sustain acceptable degradation rates. Establishing the design ROI is not a trivial task, because it depends on many factors including intrinsic permeability of the soil, soil chemistry, moisture content, and desired remediation time. The ROI should usually be determined through field pilot studies, but can be estimated from air-flow modeling or other empirical methods. Generally, the design ROI can range from 5 feet (for fine-grained soils) to 100 feet (for coarse-grained soils). For sites with stratified geology, ROI should be defined for each soil type. The ROI is important in determining the appropriate number and spacing of extraction or injection wells. Stratified soils may require special consideration in design to ensure that less-permeable strata are adequately vented.

At a site with homogeneous soil conditions, the well should be screened throughout the contaminated zone. The well screen may be placed as deep as the seasonal low water table. A deep well helps to ensure remediation of the greatest amount of soil during seasonal low groundwater conditions.

At a site with stratified soils or lithology, the screened interval can be placed at a depth corresponding to a zone of lower permeability. This placement will help ensure that air passes through this zone rather than merely flowing through adjacent zones of higher permeability.

Air flow is particularly important for soils within the capillary fringe, where a significant portion of the constituents often resides. Fine-grained soils create a thicker capillary fringe than do coarse-grained soils. The thickness of the capillary fringe can usually be determined from soil boring logs (i.e., in the capillary fringe, soils are usually described as moist or wet). The capillary fringe usually extends from one to several feet above the elevation of the groundwater table. Moisture content of soils within the capillary fringe may be too high for effective bioventing. Depression of the water table by groundwater pumping may be necessary to biovent soils within the capillary fringe.

Fluctuations in the groundwater table should also be considered. Significant seasonal or daily (e.g., tidal or precipitation-related) fluctuations may, at times, submerge some of the contaminated soil or a portion of the well screen, making it unavailable for air flow. These fluctuations are most important for horizontal wells, in which screens are placed parallel to the water table surface, as a water-table rise could occlude the entire length of the screen.

Bacteria require moist soil conditions for proper growth. Generally, soils saturated with water prohibit air flow and oxygen delivery to bacteria, while dry soils lack the moisture necessary for bacterial growth. The ideal range for soil moisture is between 40 and 85 percent of the water-holding capacity of the soil. Bioventing promotes dehydration of moist soils by means of increased air flow through the soil, whereas dehydration hinders bioventing performance and extends operation time.

The optimum pH for bacterial growth is approximately 7; the acceptable range for soil pH during bioventing is between 6 and 8. Soils with pH values outside this range prior to bioventing may require pH adjustments prior to and during bioventing operations.

Bacteria require inorganic nutrients such as ammonium (to supply nitrogen) and phosphate (to supply phosphorus) to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in site soils but, more frequently, nutrients need to be added via injection to soils to maintain bacterial populations.

**Important!** The presence of very high concentrations of organic petroleum compounds or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation. However, very low concentrations of organic material will also result in diminished levels of bacterial activity.

## Pilot Studies

In order to decide whether bioventing is likely to be highly effective, somewhat effective, or ineffective for site conditions, a pilot study can be performed. Pilot studies or bioventing may range in scope and complexity from a simple soil column test or microbial count to field respirometry tests and SVE (or injection) pilot studies. The scope of pilot testing or laboratory studies should be commensurate with the size of the area to be remediated and the reduction in constituent concentration(s) required. A list and description of commonly used laboratory and pilot-scale studies are provided below.

*Soil-Vapor Extraction and Injection Treatability Tests* are generally used to determine the ROI that an extraction well or injection well will exert in the surrounding soils, the optimum vapor flow rate and pressure (or vacuum) to be applied to the wells, and the concentration of petroleum constituents in the induced air stream. The test most often includes short-term vapor extraction or air injection from a single well while measuring the pressure effect in monitoring wells or probes spaced at increasing distances from the extraction well or the injection well. The test can assist in determining the spacing, number, and type of wells needed for the full-scale system. It is usually not economically attractive to perform this test for sites with areas smaller than 5,000 cubic yards of *in-situ* contaminated soil or for sites with soil permeabilities greater than  $10^{-8}$  square centimeters ( $\text{cm}^2$ ).

*Respirometry Studies* are generally used to determine the oxygen transport capacity of the site soils and to estimate the biodegradation rates under field conditions. The test includes short-term injection of an oxygen-inert gas mixture into a well that has been screened in the contaminated soil horizon. Carbon dioxide, inert gas (typically helium), and oxygen concentrations are measured in the injection well and surrounding wells periodically for about 1 to 5 days. The measurements are then compared to baseline concentrations of the gases prior to injection. Increases in carbon dioxide and decreases in oxygen concentrations are indications of biological metabolism of constituents; the inert gas concentration provides the baseline for these calculations. Temperature of the extracted vapor may also be monitored to



serve as an additional indicator of biological activities. Field respirometry studies are usually needed only for sites with large areas of contamination, perhaps greater than 100,000 cubic yards of *in-situ* soils requiring remediation, at sites where soil permeability is less than  $10^{-8}$  cm<sup>2</sup>, or when reductions of more than 80 percent of the initial concentrations of those COCs with vapor pressures less than 0.5 mm Hg are required.

*Laboratory Microbial Screening* tests are used to determine the presence of a population of a naturally occurring bacterium that may be capable of degrading petroleum product constituents. Samples of soils from the site are analyzed in an off-site laboratory. Microbial plate counts determine the number of colony forming units (CFU) of heterotrophic bacteria and petroleum-degrading bacteria present per unit mass of dry soil. These tests are relatively inexpensive.

*Laboratory Biodegradation Studies* can be used to estimate the rate of oxygen delivery and to determine whether the addition of inorganic nutrients is necessary. However, laboratory studies cannot duplicate field conditions, and field tests are more reliable than laboratory studies. There are two kinds of laboratory studies in this context: *slurry studies* and *column studies*.

- *Slurry studies*, which are more common and less costly, involve the preparation of numerous “soil microcosms” consisting of small samples of site soils mixed into a slurry with site groundwater. The microcosms are divided into several groups. These groups may include control groups that are “poisoned” to destroy any bacteria, non-nutrient test groups that have been provided oxygen but not nutrients, and nutrient test groups which are supplied both oxygen and nutrients. Microcosms from each group are analyzed periodically (usually weekly) for the test period duration (usually 4 to 12 weeks) for bacterial population counts and constituent concentrations. Results of slurry studies should be considered to represent optimal conditions, because slurry microcosms do not consider the effects of limited oxygen delivery or soil heterogeneity.
- *Column studies* are set up in a similar way, using columns of site soils; they may provide more realistic expectations of bioventing performance.

**Further Reading.** The text in this section is an excerpt from OUST’s publication, “How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers” (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases.  
<http://www.epa.gov/swerust1/pubs/tums.htm>

# Remediation in the Saturated Zone:

## Air Sparging



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Air sparging is a process for treating volatile and/or degradable COCs in groundwater and soil below the water table by the injection of contaminant-free air into the subsurface saturated zone, enabling a phase transfer of hydrocarbons from a dissolved state to a vapor phase. The injected air removes the COCs by volatilization and/or aerobic biodegradation. The volatilized vapors migrate into the vadose zone, where they are removed by vapor extraction or allowed to biodegrade.

The goal of air sparging is to create breakthrough conditions, so that the hydrocarbon mass is transferred from the saturated zone into the vadose zone, where it is then recovered by SVE or undergoes natural attenuation.

Air sparging is not to be confused with in-well aeration, where air is injected using a tube or other device inserted into a monitoring well. In-well aeration has a limited ROI, which is usually confined to the well casing, with little to no penetration into the surrounding water-bearing strata. During air sparging, air forced through the soil column creates "micro-channels" along paths of least resistance.

Pulsed air sparging causes the collapse of the micro-channels as air injection is stopped. The soil-grain packing arrangement is redistributed within the former micro-channel to one of a slightly higher density. When sparging is resumed, new micro-channels are formed in different locations from the former channels. As a result, oxygenated air is more evenly distributed throughout the soil column (more so than continuous sparging) by the individual sparging wells.

There are many pulsed sparging regimens, but common scenarios include operating each sparge well or group of wells in an array for a certain time period (minutes or hours) in sequence while alternating or rotating between individual wells or well groups. The pulsing not only distributes the oxygen as evenly as possible throughout the full 3-dimensional plume area, but also limits mounding (as sparging in any one specific area is temporary), and preferential groundwater gradient flow is less able to be established.

**Definition. Groundwater mounding:** Commonly, an outward and upward expansion of the free water table caused by shallow re-injection, percolation below an impoundment, or other surface recharge method (essentially, the reverse of the "cone of depression" effect created by a pumping well). Mounding can alter groundwater flow rates and direction; however, the effects are usually localized and may be temporary, depending upon the frequency and duration of the surface recharge events (Alabama State Water Program).

Mounding effects from sparging are temporary and stop when air injection is halted. Mounding occurs because of density differences between sparged and unsparged parts of the soil column, as opposed to actual groundwater elevation differences. Groundwater with air bubbles entrained in it (through the sparging process) has a lower density than unsparged groundwater.

### Advantages of Air Sparging

- Readily available equipment; easy installation.
- Implemented with minimal disturbance to site operations.
- Short treatment times (usually less than 1 to 3 years under optimal conditions).
- At about \$20–\$50/ton of saturated soil, air sparging is less costly than aboveground treatment systems.
- Requires no removal, treatment, storage, or discharge considerations for groundwater.
- Can enhance removal by SVE.

### Disadvantages of Air Sparging

- Cannot be used if free product is present (i.e., free product must be removed prior to air sparging).
- Cannot be used for treatment of confined aquifers.
- Stratified soils may cause air sparging to be ineffective.
- Some interactions among complex chemical, physical, and biological processes are not well understood.



- Lack of field and laboratory data to support design considerations.
- Potential for inducing migration of constituents.
- Requires detailed pilot testing and monitoring to ensure vapor control and limit migration.

## Application

When used appropriately, air sparging has been found to be effective in reducing concentrations of VOCs found in petroleum products at UST sites. Air sparging is generally more applicable to the lighter gasoline constituents (i.e., light aliphatics), because they readily transfer from the dissolved to the gaseous phase. Air sparging is less applicable to diesel fuel and kerosene. Appropriate use of air sparging may require that it be combined with other remediation methods (e.g., SVE or pump-and-treat). An air-sparging system can use either vertical or horizontal sparge wells. Well orientation should be based on site-specific needs and conditions (EPA 1994).

Air sparging should NOT be used if any of the following site conditions exist:

- Free product is present. Sparging in the presence of NAPL (aka “free product”) results in smearing the product throughout a larger vertical span of the soil column than it otherwise might have occupied, due to the turbulence associated with the sparging process.
- Nearby basements, sewers, or other subsurface confined spaces are present at the site. Potentially dangerous constituent concentrations could accumulate in basements unless a vapor-extraction system is used to control vapor migration.
- Contaminated groundwater is located in a confined aquifer system. Air sparging cannot be used to treat groundwater in a confined aquifer because the injected air would be trapped by the saturated confining layer and could not escape to the unsaturated zone.

Air sparging is most often used together with SVE, but it can also be used with other remediation technologies. When air sparging is combined with SVE, the SVE system creates a negative pressure in the unsaturated zone through a series of extraction wells to control the vapor plume migration. This combined system is called AS/SVE.

### Tip:

SVE is included with air sparging if the rate of sparging is high enough for air to “breakthrough” into the vadose zone to control vapors. The air that travels into the vadose zone will contain gasoline vapors generated by the mass-transfer process associated with sparging. If the rate of sparging is low enough that air doesn’t breakthrough into the vadose zone, SVE may not be required.

## Operation Principles

The effectiveness of air sparging depends primarily on two factors:

- *Vapor/dissolved-phase partitioning* of the constituents determines the equilibrium distribution of a constituent between the dissolved phase and the vapor phase. Vapor/dissolved phase partitioning is a significant factor in determining the rate at which dissolved constituents can be transferred to the vapor phase (i.e., the mass transfer rate).
- *Permeability of the soil* determines the rate at which air can be injected into the saturated zone. It is the other significant factor in determining the mass transfer rate of the constituents from the dissolved phase to the vapor phase.

In general, air sparging is more effective for constituents with greater volatility and lower solubility, and for soils with higher permeability. The rate at which the constituent mass will be removed decreases as air-sparging operations proceed and concentrations of dissolved constituents are reduced.

Soil characteristics will also determine the preferred zones of vapor flow in the vadose zone, thereby indicating the ease with which vapors can be controlled and extracted using SVE (if in use).

Stratified or highly variable heterogeneous soils typically create the greatest barriers to air sparging. Both the injected air and the stripped vapors will travel along the paths of least resistance (coarse-grained zones) and could travel a great lateral

distance from the injection point. This phenomenon could result in the contaminant-laden sparged vapors migrating outside the vapor-extraction control area.

## System Design

The essential goals in designing an air-sparging system are to configure the wells and monitoring points so as to:

- Optimize the influence on the plume, thereby maximizing the removal efficiency of the system.
- Provide optimum monitoring and vapor-extraction points to ensure minimal migration of the vapor/dissolved-phase plume and to prevent undetected migration. In shallow applications, in large plume areas, or in locations under buildings or pavement, horizontal vapor-extraction wells are very cost-effective and efficient for controlling vapor migration.

### Tip.

Horizontal wells are not usually cost-effective at LUFT sites, as their cost is 3 to 4 times the cost of a standard vertical well. Since most LUFT sites occupy a small land area (less than an acre), in most cases careful placement of vertical wells can provide a sufficient ROI such that inaccessible areas can be reached without resorting to horizontal wells. If achieving the full ROI is still difficult, vertical wells can be used in barrier applications at the downgradient edge of a property to prevent further downgradient migration without installing costly horizontal wells under buildings.

## Pilot Testing

Field pilot tests are necessary to adequately design and evaluate any air sparging system. Pilot tests should not, however, be conducted if any of the following conditions are present:

- Free product is known to exist at the groundwater table.
- Vapors can migrate uncontrolled into confined spaces, sewers, or buildings.
- The contaminant source is in a confined aquifer.

The air sparging well(s) used for pilot testing should be located in an area of no more than moderate constituent concentrations. Testing the system in areas of extremely low constituent concentrations may not provide sufficient data and, because sparging can induce migration of constituents, pilot tests are generally not conducted in areas of extremely high constituent concentrations. The air-sparging pilot study should include an SVE pilot study if SVE will be included in the design of the air sparging system (see the [SVE Pilot Study](#) section).

The placement and number of air-sparging points required to address the dissolved-phase plume is determined primarily by the permeability and structure of the soil, as these affect the sparging pressure and distribution of air in the saturated zone. Coarse-grained soils (e.g., sand, gravel) have greater intrinsic permeability than fine-grained soils (e.g., clay, silt), and it is easier to move air (and water) through more permeable soil. Greater lateral dispersion of air is likely in fine-grained soils; this can result in lateral displacement of the groundwater and contaminants if groundwater control is not maintained or cannot be maintained.

The ROI is the most important parameter to be considered in the design of the air-sparging system. The ROI is defined as the greatest distance from a sparging well at which sufficient sparging pressure and air flow can be induced to enhance the mass transfer of contaminants from the dissolved phase to the vapor phase. The ROI will help determine the number and spacing of the sparging wells. Air-sparging wells should be placed so that the overlap in their ROIs completely covers the area of contamination.

### Tip.

Careful evaluation of the ROIs of air-sparging wells and sufficient placement of enough sparging wells to fully overlap the main and downgradient plume areas eliminates the need for additional hydraulic control. In addition, pulsing the air injection and rotating between injection wells, so that no one area receives continual, sustained injection limits mounding effects and can enhance effectiveness.

The sparging air-flow rate required to provide sufficient air flow to enhance mass transfer is site-specific and is determined via pilot testing.

## Pilot Testing Procedure

The goal of a pilot test is to determine whether breakthrough conditions are possible, so that the hydrocarbon mass can be transferred from the saturated zone into the vadose zone, where it is then recovered by SVE. Detection of increased levels of hydrocarbon vapors in the observation wells compared to pre-test conditions is evidence of breakthrough.

Pilot tests should include the installation of a single sparging point, several vapor-extraction points (if SVE is to be included in the design), and soil-gas monitoring points to evaluate vapor generation rates and to define the vapor plume. Existing groundwater monitoring wells (normally not fewer than three to five wells around the plume) that have been screened above the saturated zone and through the dissolved-phase plume can be used to monitor both dissolved and vapor phase migration, to monitor for changes in dissolved oxygen, and to measure changes in the depth to the groundwater table surface. Additional vapor probes should be used to further define the vapor plume and identify any preferential migration pathways.

If SVE is to be used in the air sparging system, the first portion of the test should be conducted using vapor extraction only, without the air-sparging system being operated. This portion of the pilot test will establish the baseline vapor-extraction levels, the extent of the non-sparged vapor plume, the SVE well ROI, and the intrinsic permeability of the unsaturated zone. The air sparging portion of the test should be conducted with the sparging point operating at variable sparge pressures (e.g., 5 pounds per square inch-gauge [psig], 10 psig) and different depths (e.g., 5 feet, 10 feet below the dissolved-phase plume). It is essential that vapor equilibrium be obtained prior to changing the sparge rate or depth. When no change in vapor emission rates from baseline occurs, the air sparging system may not be controlling the sparge-vapor plume, possibly due to soil heterogeneity. Assess the potential for this problem by reviewing the site's soil lithology. During this test, the hydraulic gradient and VOC concentrations in soil vapors extracted from monitoring wells must be monitored until equilibrium is reached.

The final portion of the pilot test is the concurrent operation of the SVE pilot system and the air sparging system, if applicable. This portion of the test will determine the optimum SVE system (i.e., the number and orientation of wells) that will capture the sparged VOCs for various sparging rates. In addition, this portion of the test requires monitoring of VOC emissions, sparging pressure and flow rates, SVE vacuum and flow rates, monitoring-well vapor concentrations, and dissolved constituent concentrations (EPA 1994).

## Data Interpretation

### Tips.

Be aware of these common air-sparging issues:

- Insufficient injection rates to attain breakthrough.
- Design parameters fail to account for the radius of vapor extraction being insufficient to capture the sparged vapors (e.g., not enough vapor-extraction wells or wells spaced too far apart, incorrectly constructed too high in the vadose zone, etc.).
- Sparge wells screened in zones with too-low permeability (sparging cannot occur) or screened too high in the aquifer (deeper plume components at the base of the aquifer will not be remediated by the sparging process).
- Vadose zone is substantially less permeable than the sparged depth interval – vapors will not be able to break through, and the plume is forced laterally outwards.
- Silty soils overlying sands may experience delayed breakthrough or the site may have a relatively large ROI of air sparging, but if the permeability difference is too great, breakthrough never occurs and the plume channels/spreads downgradient.

Increased vapor concentrations and/or dissolved oxygen (DO) levels in observation wells after test initiation are evidence that the ROI includes the observation well. Measuring the ROI on a basic level consists of extrapolating data based on the distance between the injection and observation wells. For example, if the observation well is 15 feet from the injection well and vapors are observed in the well after initiating the test, the ROI is at least 15 feet. Various software programs and/or calculations can be used to determine more precisely the expected lateral ROI.

Interpretation of the ROI includes consideration of lithologic heterogeneity and the potential for air to flow through preferential migration pathways. Sands tend to have a smaller ROI than silts and clays due to increased permeability; that is, injection meets with less resistance. The ROI of air sparging is inversely proportional to increases in permeability,

whereas the radius of vapor-extraction influence is directly proportional to increases in permeability. The limitations of both technologies are met in clay soils, which have very small ROIs to vapor extraction, and are very difficult to sparge without artificially increasing permeability, except at very low flow rates.

The vertical radius of sparge influence is an inverted “V” upwards from the tip of the sparge point, which diminishes upwardly, proportional to the friction loss experienced with relation to the soil type. A thick zone requiring treatment may require sparge well clusters installed to various depths to best treat the entire vertical extent of the plume.

## Remediation Application

The combined sparge ROI should fit within the combined radius of vapor-extraction influence to prevent sparged vapors escaping effective capture. The rate of SVE must be sufficient to capture all of the sparged vapors.

While vapor extraction will be constant during air injection in order to contain the sparged vapors, pulsing air injection takes advantage of soil-grain packing and soil mechanics, and substantially increases the effectiveness of the sparging process.

Injection of air creates temporary flow pathways in the soil, changing the grain-packing structure such that grains are closer together during the time air is passing through the flow pathway. Once sparging is stopped, the air channels collapse, forming a less-permeable structure in the soil. The next time air is injected, the air, following the path of least resistance, creates a new flow pathway in a different part of the subsurface.

Utilizing repeated pulsing, the overall surface area of soil exposed to the sparging process is exponentially increased, whereas sustained injection without pulsing simply transports the air through a single set of flow pathways. Pulsing therefore dramatically increases the efficiency of air sparging. Pulse timing is lithology-dependent, but can range from a few minutes per event to several hours. Full-scale application may involve pulsing each injection well in turn (higher per-well injection pressures) or pulsing all wells at the same time for a specified duration (more areal coverage, but lower injection pressure per well point).

**Further Reading.** The text in this section is an excerpt from OUST’s publication, “How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers” (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases.  
<http://www.epa.gov/swerust1/pubs/tums.htm>

# Remediation in the Saturated Zone:

## Biosparging



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Biosparging is an *in-situ* groundwater remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the saturated zone. Through biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms. Biosparging can be used to reduce concentrations of petroleum constituents that are dissolved in groundwater, adsorbed to soil below the water table, and within the capillary fringe. Although constituents adsorbed to soils in the unsaturated zone can also be treated by biosparging, bioventing is typically more effective for this situation.

When volatile constituents are present, biosparging is often combined with SVE or bioventing and can also be used with other remediation technologies. When biosparging is combined with vapor extraction, the vapor-extraction system creates a negative pressure in the vadose zone through a series of extraction wells that control the vapor plume migration.

### Advantages of Biosparging

- Readily available equipment; easy installation.
- Implemented with minimal disturbance to site operations.
- Short treatment times, 6 months to 2 years, under optimal conditions.
- Cost competitive.
- Enhances the effectiveness of air sparging for treating a wider range of petroleum hydrocarbons.
- Requires no removal, treatment, storage, or discharge of groundwater.
- Low air-injection rates minimize potential need for vapor capture and treatment.

### Disadvantages of Biosparging

- Can only be used in environments where air sparging is suitable (i.e., uniform and permeable soils, unconfined aquifer, no free-phase hydrocarbons, no nearby subsurface confined spaces).
- Some interactions among complex chemical, physical, and biological processes are not well understood.
- Lack of field and laboratory data to support design considerations.
- Potential for inducing migration of constituents.

### Application

When used appropriately, biosparging is effective in reducing concentrations of petroleum products at UST sites. Biosparging is most often used at sites with mid-weight petroleum products (e.g., diesel fuel, jet fuel); lighter petroleum products (e.g., gasoline) tend to volatilize readily and to be removed more rapidly using air sparging. Heavier products (e.g., lubricating oils) generally take longer to biodegrade than lighter products, but biosparging can still be used at these sites.

The existing literature contains case histories describing both the success and failure of biosparging; however, since the technology is relatively new, there are few cases with substantial documentation of performance.

### Operation Principles

The biosparging process is similar to air sparging. However, while air sparging removes constituents primarily through volatilization, biosparging promotes biodegradation of constituents rather than volatilization (generally by using lower flow rates than are used in air sparging). In practice, some degree of volatilization and biodegradation occurs when either air sparging or biosparging is used.

The effectiveness of biosparging depends primarily on two factors:

- The permeability of the soil, which determines the rate at which oxygen can be supplied to the hydrocarbon-degrading microorganisms in the subsurface.



- The biodegradability of the petroleum constituents, which determines both the rate at which and the degree to which the constituents will be degraded by microorganisms.

In general, the type of soil and porosity will determine its permeability. Fine-grained soils (e.g., clays and silts) have lower permeabilities than coarse-grained soils (e.g., sands and gravels). More-permeable soils allow for easier air flow.

Bacteria require a carbon source for cell growth and an energy source to sustain metabolic functions required for growth. The biodegradability of a petroleum constituent is a measure of how well it can be metabolized by hydrocarbon-degrading bacteria or other microorganisms. Petroleum constituents are generally biodegradable, regardless of their molecular weight, as long as indigenous microorganisms have an adequate supply of oxygen and nutrients. For heavier constituents (which are generally less volatile and less soluble than lighter constituents), biodegradation will exceed volatilization as the primary removal mechanism, even though biodegradation is generally slower for heavier constituents than for lighter constituents.

The presence of very high concentrations of petroleum organics or heavy metals in site soils can be toxic or inhibit the growth and reproduction of bacteria responsible for biodegradation. Conversely, very low concentrations of organic material will result in diminished levels of microbial activity.

Other factors that influence the efficacy of biosparging are those that affect the growth and viability of the microorganisms which degrade petroleum hydrocarbons. These factors include:

- Temperature of the groundwater
- pH levels
- Presence of sufficient electron acceptors
- Nutrient concentrations

Bacterial growth rate is a function of temperature. Microbial activity has been shown to significantly decrease at temperatures below 10°C. The microbial activity of most bacteria important to petroleum hydrocarbon biodegradation also diminishes at temperatures greater than 45°C. Within the range of 10°C to 45°C, the rate of microbial activity typically doubles for every 10°C rise in temperature.

To support bacterial growth, the pH should be within the 6 to 8 range, with a value of about 7 (neutral) being optimal. If the groundwater pH is outside this range, it is possible to adjust the pH prior to and during biosparging operations. However, pH adjustment is often not cost-effective, because the natural buffering capacity of the groundwater system generally necessitates continuous adjustment and monitoring throughout the biosparging operation. In addition, efforts to adjust pH may lead to rapid changes in pH, which are also detrimental to bacterial activity.

For biosparging applications directed at petroleum products, bacteria that use oxygen as an electron acceptor (that is, they metabolize organic contaminants aerobically) are most important in the degradation process, because they can degrade these products more rapidly than organisms which use other electron acceptors. The rate of biodegradation will depend, in part, on the supply of oxygen to the contaminated area, because aerobic metabolism is much faster than anaerobic metabolism. When there is an insufficient amount of dissolved oxygen available, organisms which can use other electron acceptors may degrade the contaminants, but at slower rates.

Bacteria require inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the aquifer but, more frequently, nutrients need to be added to maintain adequate bacterial populations. Excessive amounts of certain nutrients (e.g., phosphate and sulfate), however, can repress metabolism.

**Important!** Biosparging should NOT be used if the following site conditions exist:

- Free product is present. Biosparging can create groundwater mounding, which could potentially cause free product to migrate and contamination to spread.
- Nearby basements, sewers, or other subsurface confined spaces are present at the site. Potentially dangerous constituent concentrations could accumulate in basements unless a vapor-extraction system is used to control vapor migration.
- Contaminated groundwater is located in a confined aquifer system. Biosparging cannot be used to treat groundwater in a confined aquifer because the injected air would be trapped by the saturated confining layer and could not escape to the unsaturated zone.

## System Design

There are several factors to consider when designing a biosparge system. The placement and number of biosparge points required to aerate the dissolved-phase plume is determined primarily by the permeability and structure of the soil, as these affect the sparging pressure and distribution of air in the saturated zone.

The *bubble radius* (analogous to the ROI for air-sparging systems) is defined as the greatest distance from a sparging well at which sufficient sparge pressure and air flow can be induced to enhance the biodegradation of contaminants. The bubble radius will determine the number and spacing of the sparging wells. The bubble radius should be determined based on the results of pilot tests. The bubble radius depends primarily on the hydraulic conductivity of the aquifer material in which sparging takes place. Other factors that affect the bubble radius include soil heterogeneities and differences between the lateral and vertical permeability of the soils. Generally, the design bubble radius can range from 5 feet for fine-grained soils to 100 feet for coarse-grained soils.

The *Sparging Air Flow Rate* required to provide sufficient air flow to enhance biological activity is site-specific and will be determined via the pilot test. Typical air-flow rates are much lower than for air sparging, ranging from 3 to 25 standard cubic feet per minute (scfm) per injection well. Pulsing of the air flow (i.e., turning the system on and off at specified intervals) may provide better distribution and mixing of the air in the contaminated saturated zone, thereby allowing for greater contact with the dissolved phase contaminants. If a vapor-extraction system is used, it should have a greater flow capacity and greater area of influence than the biosparging system. Typically the SVE rates range from 1.25 to 5 times greater than the biosparging rate.

The *Sparging Air Pressure* is the pressure at which air is injected below the water table. Injection of air below the water table requires pressure greater than the static water pressure (1 psig for every 2.3 ft of hydraulic head) and the head necessary to overcome capillary forces of the water in the soil pores near the injection point. A typical system will be operated at approximately 10 to 15 psig. Excessive pressure may cause fracturing of the soils and create permanent air channels that can significantly reduce biosparging effectiveness.

The *Nutrient Formulation and Delivery Rate* (if needed) will be based on the results of the laboratory tests and pilot study results. Common nutrient additions include nitrogen (in an aqueous solution containing ammonium ions) and phosphorus (in an aqueous solution containing phosphate ions). Note that state regulations may either require permits for nutrient injection or prohibit them entirely.

The *Initial Constituent Concentrations* will be measured during pilot-scale studies. They establish a baseline for estimating the constituent mass removal rate and the system operation time requirements. In addition, they will help to determine whether vapor treatment will be required.

The *Initial Concentrations of Oxygen and CO<sub>2</sub>* in the saturated zone will be measured during pilot studies. They are used to establish system operating requirements, to provide baseline levels of subsurface biological activity, and to allow measurement of the system's progress.

**Further Reading.** The text in this section is an excerpt from OUST's publication, "How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers" (EPA 1994). This publication provides extensive detail on technologies for remediation of petroleum releases.  
<http://www.epa.gov/swerust1/pubs/tums.htm>



# Remediation in the Saturated Zone:

## *In-Situ* Groundwater Ozone Sparging



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Ozone (O<sub>3</sub>) sparging is an *in-situ* groundwater chemical oxidation technology. This technology is an enhanced form of air sparging which involves the injection of ozone into the groundwater below the water table. The injected ozone migrates outward and upward, causing a chemical oxidation process to take place. As the ozone travels through the saturated zone, the chemical oxidation causes the destruction of LUFT COCs into carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O).

### Advantages to Ozone Sparging

- Effective in treating MTBE, TBA, and other oxygenates, may be beneficial in treating BTEX when combined with other technologies.
- Can be delivered continuously as opposed to batch applications typically associated with other chemical oxidation techniques, which delivers the opportunity for greater oxidation.
- Ozone is generated on site, so storage and transportation of dangerous chemicals is not needed
- Short treatment times
- Can stimulate biodegradation as an after-effect

### Disadvantages to Ozone Sparging

- Not effective in clays and tight soils
- Low-flow injection may be insufficient to remediate adsorbed-phase BTEX and TPH below the soil/water interface.
- If trivalent chromium (Cr[III]) is present in the soil in sufficient quantities and/or redox conditions are present which do not support return to background state outside the immediate area of injection, the possibility of creating hexavalent chromium (Cr[VI]) and/or other byproduct species in unacceptable quantities exists

### Application

When used appropriately, ozone sparging can be effective in reducing concentrations of oxygenate LUFT COCs, including MTBE and TBA, and can be beneficial at degrading BTEX and TPH. Ozone-air sparging destroys dissolved COCs by three key processes. First, when air is bubbled through groundwater in soil pores, dissolved VOCs transfer from liquid to gas phase in accordance with Henry's Law. Second, ozone in the sparge bubbles reacts extremely rapidly with VOCs, destroying them in the process. Thirdly, residual oxygen from the reaction encourages bioremediation, which consumes the breakdown products and converts them to carbon dioxide and water (Schwartz, et al. 2005).

### Operational Principles

The use of ozone is different from most oxidation processes: ozone can be injected as a gas. This provides the opportunity to apply the treatment continuously rather than in batch applications. Ozone sparging is best applied at sites with at least moderate soil permeability. Sparging into predominantly clay soils is not likely to be effective unless the permeability is increased artificially by fracturing or other means. Lithology above and below the screened interval of the sparge well influences the outcome as well.

### System Design

For groundwater remediation, ozone is transported beneath the groundwater table via injection wells. An air compressor draws in ambient air which is passed through an oxygen concentrator. The oxygen concentrator removes nitrogen from the air stream and delivers pure oxygen to an ozone generator. The ozone generator uses a high-voltage electrical current to convert oxygen to ozone. Another air compressor is often then used to blend in ambient air with the produced ozone, allowing the ozone to be injected into the subsurface at typical flow rates of 1 to 4 cfm and up to 10 cfm at pressures up to 50 pounds per square inch (psi) and various concentrations of ozone. The mixture of air and ozone is usually injected into the subsurface through micro-porous oxidation points via an oxidation port manifold. A field programmable logic controller (PLC) with an interface panel viewer is used to control the manifold, allowing field personnel to enable and disable

oxidation points, switch between ozone and oxygen injection (if the equipment used has this capability), set lag time between sparge cycles, and set sparge duration (Plummer, et al.)

Injection well screens should be located with the base of the well coinciding with the base of the plume. A minimum of 5 feet of groundwater should be present above the top of the injection point's sand filter pack to minimize short-circuiting to the surface. In addition, the bentonite seal should be installed so as to prevent "bridging" (see below). For deeper plumes, several injection wells may have to be installed at progressively shallower depths. The upward vertical limit of sparging is generally between 15 to 20 feet, depending on lithology.

**Tip** Injection well construction (typical): 1-inch inner diameter (ID), Schedule 80 Polyvinyl Chloride (PVC) connected to a 1.5-inch diameter by 18-inch-long gas diffuser. Some manufacturers of ozone-generating equipment recommend use of stainless-steel wells and diffusers. If the remediation effort is expected to last more than 5 years, it is recommended that stainless-steel wells be used.

A sand pack of #2/16 or other appropriate sand is placed from the base of the well to at least 1 foot above the top of the gas diffuser, with at least 3 feet of bentonite chips hydrated in place overlying the top of the filter pack. A neat cement grout seal is then placed from the top of the upper bentonite layer to approximately 1 foot below grade. A wellhead connection is placed on top of the riser pipe, with an appropriate box set at grade.

In order for ozone sparging to be effective, adequate contact between oxidants and COCs is needed. Accounting for subsurface heterogeneities or preferential flow paths is needed to ensure that there are no pockets of untreated contaminants. Ozone injection points are strategically installed across the area of impact to provide proper overlap of the injection area or ROI. The ROI is usually determined by conducting an ozone sparging pilot test.

## Pilot Test

The goal of an ozone sparging pilot test is to inject ozone below the water table and determine whether and how far ozone is migrating through the saturated zone, whether oxidation of COCs is occurring, and to determine the ROI. This is ascertained by installing injection points and monitoring groundwater conditions in adjacent monitoring wells (observation wells).

For pilot-testing purposes, injection test wells should be no more than 15 to 20 feet up- or cross-gradient from at least one nearby groundwater monitoring well (ideally located in the area of highest concentrations). Spacing at greater distances may show no results during the test.

Nearby groundwater monitoring well(s) are used as observation points to evaluate the effects of the test.

**Important!** It is important to consider that ozone has the potential to oxidize UST tanks, underground lines, or equipment. It is imperative that all components of the system be ozone-compatible, or that ozone injection be conducted sufficiently distant from the fueling system or other underground facilities with which ozone may react. Compatible materials include stainless steel, Teflon, Kynar, Viton, and Schedule 80 PVC. High-density polyethylene (HDPE) and natural rubbers are not compatible and should be avoided.

In addition, measurements of groundwater elevation, pH, oxidation/reduction potential (ORP), electrical conductivity (EC), DO, ambient gasoline-vapor concentrations, and temperature are often collected from both the observation wells and injection wells prior to initiating testing. Changes in these parameters are indicators of chemical oxidation occurring, as discussed in further detail in the "[Data Analysis and Interpretation of Pilot Test](#)" section of this chapter.

During initial test start-up, separate baseline DO concentrations, air-flow rate, temperature, and depth-to-water measurements (field data) should be recorded for each injection point and observation well. Screened interval data for new and existing wells should be evaluated prior to the test. Equipment sparge manifold and wellhead equipment should allow for concurrent reporting of isolated field data measurements from individual extraction wells.

## Pre-Test Sampling

Before initiating the test, sample the groundwater monitoring wells to be used as observation points for the COCs associated with the site and any by-product species (such as hexavalent chromium and/or bromide/bromate ratios) with the potential to be generated during the test, using standard sampling methods.

Many agencies are concerned with by-product creation during oxidant injection of toxic metals as a by-product during oxidation such as hexavalent chromium, discussed in further detail in the [“Ozone By-Product Evaluation”](#) section of this chapter below. If the site is located in an area where mafic minerals are likely contributors to local soils, or if required by the agency, the following additional pre-test analyses should be considered: manganese, total chromium, vanadium, selenium, and molybdenum by EPA Method 200.8; bromide and bromate by EPA Method 300.1; and hexavalent chromium by EPA Method 7199.

At many sites, hexavalent chromium created as a by-product of ozone injection may be found to be ephemeral and/or limited to the immediate area of injection. Away from the injection point and/or after injection ceases, at these sites the hexavalent chromium will revert back to the trivalent state, as documented by groundwater testing.

Ozone injection can often stimulate biodegradation as an after-effect of the injection process: un-reacted ozone degrades to oxygen. To evaluate the inherent potential of a site to undergo biodegradation related to increased oxygen levels, pre-test sampling should also include testing for the following biodegradation indicators and common natural attenuation parameters: heterotrophic plate count (HPC) (a screening check for aerobic bacterial activity), nitrate, sulfate, ferrous iron (Fe[II]), alkalinity, and specific conductivity.

If biodegradation is desired as a by-product of ozone injection, a one-day test may not show measurable changes; however, the presence of some aerobic bacteria is usually evidence of the potential for the population to increase in response to additional oxygen.

Inorganic compounds and other organic compounds such as chlorinated solvents can increase the amount of ozone needed to destroy LUFT COCs. Inorganic compounds are oxygen receptors which, if present, will create an additional demand on ozone. Chlorinated solvents require larger quantities for complete oxidation to occur than do petroleum hydrocarbons. It is important to understand whether these chemicals are present to determine the amount of ozone needed. If previous data have not been collected for these constituents, groundwater analysis is recommended.

## Typical Test Process

During ozone injection, DO and ORP levels are monitored frequently (e.g., every 15 minutes or as practical, based on the number of observation wells being used) in the observation wells, along with depth to water, pH, EC, and temperature. In addition, a PID or FID is used to monitor for the presence of gasoline vapors in the observation wells, and an ozone meter is also recommended to check for the presence of ozone vapors in the observation wells. Such vapors indicate that ozone is migrating in the subsurface from the injection points to the observation wells.

Several different injection pressures should be attempted during a one-day event to obtain a range of data readings, and the various injection pressures recorded as part of the data set. It is not usually desirable to sparge ozone to “breakthrough” pressure (which is conversely the main goal of traditional air-sparging), so the maximum optimal pressure during the test is usually one which is found to be slightly lower than breakthrough. The reason for this is that, once in the vadose zone, ozone vapors require extraction and treatment using SVE equipment, which often reacts negatively to the ozone. Also, breakthrough increases the chances that ozone will migrate to the ground surface, posing issues with surface and atmospheric receptors. During the test, this is accomplished by detecting breakthrough and then reducing the injection pressure. “Breakthrough” is indicated when, as compared with pre-test levels, increased concentrations of either 1) gasoline vapors or 2) gaseous ozone is detected in the observation wells during the test. The presence of gaseous ozone, in particular in the observation wells, is evidence that vapor-phase ozone has “broken through” into the vadose zone from the saturated zone.

DO, ORP, depth to water, pH, EC, and temperature should also be monitored for 2 to 3 hours after the last injection and 24 hours after the last injection. As both DO and ORP meters tend to be very sensitive and lose calibration during the test, calibration of DO and ORP meters is recommended a minimum of two times during the test.

Mobile ozone-injection units are available from various equipment rental companies and/or ozone injection system manufacturers. A typical ozone generator is capable of delivering 1.0 to 20.0 lb of ozone per day, up to 6% concentration by weight, with a variable delivery flow rate between 0.5 and 10 cfm.

## Post-Test Analyses

One week after the completion of the ozone injection pilot test, follow-up groundwater samples should be collected from the same observation wells and analyzed for the same suite of constituents as was analyzed in the pre-test sampling.

### Tips.

Be aware of these common Ozone and/or Oxygen Sparging issues:

- Undersized ozone generator.
- Poor design of ozone delivery system manifold. Does not allow for concurrent reporting of isolated field data measurements from individual extraction wells.
- Poor quality piping and wellhead connectors. Piping and connectors exposed to ozone should be corrosion resistant.
- Sparge wells screened in low-permeability zones or in the wrong part of the water-bearing zone.
- Detecting either gasoline or ozone vapors in observation well(s) during the test indicates that the injection pressure is sufficient to have induced breakthrough. As mentioned in the discussion, this is not desirable.

## Data Analysis and Interpretation of Pilot Test

Increased DO and ORP levels in observation wells after test initiation are evidence that the ROI includes the observation well. Measuring the ROI on a basic level consists of extrapolating data based on the distance between the injection and observation wells. For example, if the observation well is 15 feet from the injection well and a DO increase is observed, the ROI is at least 15 feet.

Various software programs and/or calculations can be used to determine more precisely the expected lateral ROI. Interpretation of the ROI includes consideration of lithologic heterogeneity and the potential for ozone to flow through preferential migration pathways.

Conditions that do not support traditional air sparging (such as low-permeability soils overlying high-permeability soils) can support ozone sparging by creating a cap to ozone vapors migrating into the vadose zone.

Decreased dissolved-gasoline concentrations in observation wells or changing ratios of oxygenates indicate that ozone injection has destroyed gasoline within the distance between the injection and observation wells. In particular, MTBE will convert to TBA as a result of partial oxidation. If concentrations of MTBE were higher before the test and TBA was lower, and these ratios reverse, this is evidence of successful (although partial) oxidation. Sustained injection should result in TBA concentration declines as the reaction is given a chance to break down the TBA.

## Ozone By-Product Evaluation

Many regulators are concerned about the creation of by-products such as hexavalent chromium (Cr(VI)) during ozone injection.

There are several risk factors which can predict whether ozone injection at a site will create Cr(VI). The primary risk factor is the presence of significant concentrations of trivalent (Cr(III)) in the soil. If there is no or low Cr(III) in the soil, Cr(VI) will not be created by reactions between site soils and injected ozone.

In addition to the presence of Cr(III), the following site conditions may predispose a site to the creation of Cr(VI) under oxidizing conditions:

- Site location in a sedimentary basin with Franciscan assemblage or similar type source rocks. Soils from these type of rocks are usually rich in both manganese and Cr(III). Manganese is a catalyst for Cr(VI) creation, but is not detectable in groundwater (not soluble). The presence of manganese at a site is determined through soil sampling.
- Low background humus/organics in the soil.
- Low levels of electron acceptors.

A study entitled "Remediation of Chromium(VI) in the Vadose Zone: Stoichiometry and Kinetics of Chromium(VI) Reduction by Sulfur Dioxide," prepared by Min Ahn and dated August 2003, states, "[the] Cr(VI) can be reduced to Cr(III) by numerous

reductants including Fe(II), organic matter and reduced sulfur compounds.” This study shows that the presence of humus or alternate electron acceptors suppresses the conversion of Cr(III) into Cr(VI), as does the presence of reducing conditions.

If a site is documented to have conditions which result in the creation of persistent by-products at detrimental levels, an alternate form of remediation should be considered, or a modification of the ozone injection process should be discussed with the regulator.

## Remediation Application

Sometimes dissolved-gasoline concentrations will temporarily increase either in the injection wells or the observation wells as a response to testing. This also indicates some measure of success, as the increase is due to gasoline formerly adsorbed onto soil particles being desorbed through reaction with ozone and transferred to the dissolved state. This is most often observed after installation of an ozone injection system and following several weeks or more of operation. Sustained injection with higher concentrations of ozone should result in declining dissolved gasoline concentrations over time.

For bacterial activity, as mentioned, a one-day test may not create much change. Bacterial growth normally responds best to sustained injection (for example, a series of injection events, or initiation of full-scale remediation). Bacterial colonies usually take between 3 and 6 months to become established after sustained addition of oxygen.

# Remediation in the Saturated Zone:

## *In-Situ* Groundwater Bioremediation



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*In-situ* groundwater bioremediation is a technology that encourages growth and reproduction of indigenous microorganisms to enhance the biodegradation of organic constituents in the saturated zone. *In-situ* groundwater bioremediation can effectively degrade organic constituents which are dissolved in groundwater and adsorbed onto the aquifer matrix.

### Advantages of Bioremediation

- Remediates contaminants that are adsorbed onto or trapped within the geologic materials of which the aquifer is composed, along with contaminants dissolved in groundwater.
- Application involves equipment that is widely available and easy to install.
- Creates minimal disruption and/or disturbance to ongoing site activities.
- Time required for subsurface remediation may be shorter than for other approaches.
- Generally recognized as being less costly than other remediation options.
- Can be combined with other technologies (e.g., bioventing, SVE) to enhance site remediation.
- In many cases, this technique does not produce waste products that must be disposed.

### Disadvantages of Bioremediation

- Injection wells and/or infiltration galleries may become plugged by microbial growth or mineral precipitation.
- High concentrations (TPH greater than 50,000 ppm) of low-solubility constituents may be toxic to microorganisms and/or not bioavailable.
- Difficult to implement in low-permeability aquifers.
- May require continuous monitoring and maintenance.
- Remediation may only occur in more permeable layers or channels within the aquifer.

### Application

*In-situ* groundwater bioremediation can be effective for the full range of petroleum hydrocarbons. While there are some notable exceptions (e.g., MTBE), short-chain, low-molecular-weight, more water-soluble constituents are degraded more rapidly and to lower residual levels than are long-chain, high-molecular-weight, less-soluble constituents. Recoverable free product should be removed from the subsurface prior to operation of the *in-situ* groundwater bioremediation system. This will mitigate the major source of contaminants as well as reduce the potential for smearing or spreading high concentrations of contaminants.

*In-situ* bioremediation of groundwater can be combined with other saturated-zone remediation technologies (e.g., air sparging) and vadose-zone remediation operations (e.g., SVE, bioventing).

### Operation Principles

Bioremediation generally requires a mechanism for stimulating and maintaining the activity of microorganisms. This mechanism is usually a delivery system for providing one or more of the following: An electron acceptor (oxygen, nitrate); nutrients (nitrogen, phosphorus); and an energy source (carbon). Generally, electron acceptors and nutrients are the two most critical components of any delivery system.

Nutrient injection systems may not be necessary at all if the groundwater contains adequate amounts of nutrients such as nitrogen and phosphorus. Microorganisms require inorganic nutrients such as nitrogen and phosphate to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the aquifer but, more frequently, nutrients need to be added to maintain adequate bacterial populations.

In a typical *in-situ* bioremediation system, groundwater is extracted using one or more wells and, if necessary, treated to remove residual dissolved constituents. The treated groundwater is then mixed with an electron acceptor and nutrients



(and other constituents if required), and re-injected upgradient of or within the contaminant source. Infiltration galleries or injection wells may be used to re-inject treated water. Ideally, a “closed-loop” system would be established. This ideal system would continually recirculate the water until cleanup levels had been achieved. An alternative to the “closed-loop” system is to mix the electron acceptor and nutrients with fresh water instead of the extracted groundwater. Extracted water that is not re-injected must be discharged, typically to surface water, sanitary sewer, or to a publicly owned treatment works (POTW).

## System Design

*In-situ* bioremediation can be implemented via a number of treatment modes, including:

- Aerobic (oxygen respiration)
- Anoxic (nitrate respiration)
- Anaerobic (non-oxygen, non-nitrate respiration)
- Co-metabolic

Aerobic treatment has been proven most effective in reducing contaminant levels of aliphatic (e.g., hexane) and aromatic petroleum hydrocarbons (e.g., benzene, naphthalene) typically present in gasoline and diesel fuel. In aerobic treatment, groundwater is oxygenated, some examples include:

- Direct sparging of air or oxygen through an injection well
- Saturation of water with air or oxygen prior to re-injection
- Addition of hydrogen peroxide directly into an injection well or into re-injected water
- Addition of high-oxygen solution

Whichever method of oxygenation is used, it is important to ensure that oxygen is being distributed throughout the area of contamination. Anoxic, anaerobic, and co-metabolic modes are sometimes used for remediation of non-hydrocarbon compounds, such as chlorinated solvents, but are generally slower than aerobic respiration in breaking down petroleum hydrocarbons.

The key parameters that determine the effectiveness of *in-situ* groundwater bioremediation are:

- Hydraulic conductivity of the aquifer, which controls the distribution of electron acceptors and nutrients in the subsurface.
- Biodegradability of the petroleum constituents, which determines both the rate and degree to which constituents will be degraded by microorganisms.
- Location of petroleum contamination in the subsurface.
- Accurate geology thru continuous data to give an accurate CSM.

For biodegradation to be effective, contaminants must be dissolved in groundwater or adsorbed onto more permeable sediments within the aquifer.

In general, the aquifer medium will determine hydraulic conductivity. Fine-grained media (e.g., clays, silts) have lower intrinsic permeability than coarse-grained media (e.g., sands, gravels). Bioremediation is generally effective in permeable (e.g., sandy, gravelly) aquifer media. However, depending on the extent of contamination, bioremediation can also be effective in less-permeable silty or clayey media. In general, an aquifer medium of lower permeability will require more time to remediate than a more permeable medium.

The location, distribution, and disposition of petroleum contamination in the subsurface can significantly influence the likelihood of success for bioremediation. This technology generally works well for dissolved contaminants and contamination adsorbed onto higher permeability sediments (sands and gravels). However, if the majority of contamination is

- 1) in the unsaturated zone,
- 2) trapped in lower permeability sediments, or
- 3) outside the “flow path” for nutrients and electron acceptors,

this technology will have reduced or even no impact.

Soil structure and stratification are important to *in-situ* groundwater bioremediation because they affect groundwater flow rates and patterns when water is extracted or injected. Structural characteristics such as micro-fracturing can result in



higher permeabilities than expected for certain soils (e.g., clays). In this case, however, flow will increase in the fractured media but not in the unfractured media. The stratification of soils with different permeabilities can dramatically increase the lateral flow of groundwater in the more-permeable strata while reducing the flow through less-permeable strata. This preferential flow behavior can lead to reduced effectiveness and extended remediation times for less-permeable strata.

The biodegradability of a petroleum constituent is a measure of how well it can be metabolized (or co-metabolized) by hydrocarbon-degrading bacteria or other microorganisms. The chemical characteristics of the contaminants will dictate their biodegradability. The biodegradability of organic constituents depends on their chemical structures and physico-chemical properties (e.g., water solubility partition coefficient). Highly soluble organic compounds with low molecular weights will tend to be more rapidly degraded than slightly soluble compounds with high molecular weights. The low water solubilities of the more complex compounds render them less bioavailable to petroleum-degrading organisms. Consequently, the larger, more complex chemical compounds may be slow to degrade or may even be recalcitrant to biological degradation (e.g., asphaltenes in No. 6 fuel oil).

Extreme pH values (i.e., less than 5 or greater than 10) are generally unfavorable for microbial activity. Typically, optimal microbial activity occurs under neutral pH conditions (i.e., in the range of 6 to 8). The optimal pH is site-specific. For example, aggressive microbial activity has been observed at lower pH conditions outside this range (e.g., 4.5 to 5) in natural systems. Because indigenous microorganisms have adapted to the natural conditions where they are found, pH adjustment, even toward neutral, can inhibit microbial activity. If man-made conditions (e.g., releases of petroleum) have altered the pH outside the neutral range, pH adjustment may be needed. If the pH of the groundwater is too low (too acidic), lime or sodium hydroxide can be added to increase the pH. If the pH is too high (too alkaline/caustic), then a suitable acid (e.g., hydrochloric, muriatic) can be added to reduce the pH. Changes to pH should be closely monitored, because rapid changes of more than 1 or 2 units can inhibit microbial activity and may require an extended acclimation period before microbes are able to resume activity.

Extraction wells are generally necessary to achieve hydraulic control over the plume to ensure that it does not spread contaminants into areas where contamination did not previously exist or accelerate the movement toward receptors. Placement of extraction wells is critical, especially in systems that also use nutrient injection wells or infiltration galleries. These additional sources of water can alter the natural groundwater flow patterns, which can cause the contaminant plume to move in an unintended direction or at an unintended rate. Without adequate hydraulic control, this situation can lead to worsening of the original condition and complicate or extend the cleanup.

The goal of the remediation process is to sustain DO levels at 3 ppm, which is the minimum threshold for aerobic degradation.

## General Procedures

Pre-test measurements include DO and other monitored parameters, including HPC, as an approximation of expected bacterial activity. These data establish “baseline” or pre-remediation background conditions.

The absence of indigenous bacteria may indicate a lower potential for success in any given environment. In particular, clean sands may be less amenable to aerobic biodegradation due to a lack of substrate for bacteria to colonize.

A general procedure for oxygen uptake studies is as follows:

- 1) Install a sparging well in the area of proposed treatment.
- 2) Conduct a routine sparging test to evaluate the ROI. The radius of oxygen diffusion may be slightly higher than the mechanical radius of sparging influence if a diffusion gradient is established between areas of higher and lower relative oxygen content.
- 3) Inject oxygen into the sparging well until oxygen saturation is attained (i.e., DO levels in excess of 20 ppm). Periodic checks of oxygen levels in the injection well can be made within several hours, days, or weeks of the initial injection.

## Data Analysis and Interpretation

The rate of oxygen consumption by the bacteria is calculated on a general basis, depending on how long it takes DO levels to drop either to below 3 ppm or to pre-test levels. The timing of subsequent injections is the frequency required to maintain oxygen in the injection well at the desired steady-state level.

Checking the HPC against pre-test conditions is a *direct indicator* of whether colonies are growing in response to additional oxygen. Declining dissolved-gasoline concentrations are an *indirect indicator* of remediation success.

If dissolved-gasoline concentrations do not show a decline in response to oxygen injection after a few months, either the amount of oxygen is insufficient or biodegradation is not viable for a particular site. Reasons for non-viability can include the hydrocarbon mass being too large or too high in concentration, other background conditions interfering with bacterial growth, or the lack of sufficient substrate for colony growth.

**For Example.** Peat-bog soils or other natural sources of biological material may preferentially biodegrade in the presence of surplus oxygen. In this case, the oxygen intended to degrade the petroleum contamination is consumed prior to contact with those microorganisms.

## Remediation Application

It normally takes six months to a year to fully establish a bacterial colony sufficient to consume significant quantities of hydrocarbon mass. Wells are spaced in accordance with the calculated ROI to provide full plume coverage, or are spaced in a barrier arrangement to prevent/limit off-site downgradient migration.

Sometimes a temporary increase in dissolved gasoline concentrations may be observed as the bacterial colonies become established: biosurfactants generated as a by-product of bacterial activity cause the desorption of adsorbed constituents from saturated-zone soil particles. This is most common at sites where the majority of the soil plume mass is below the water table. With sustained conditions hospitable to colony growth, the temporary increase in dissolved gasoline usually dissipates quickly. The installation of downgradient sentry monitoring wells to watch for plume detachment may be necessary in some cases.

# Remediation in the Saturated Zone:

## Groundwater Extraction



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### Groundwater Extraction

Groundwater extraction is a common method for treating contaminated groundwater at LUFT sites. The two most common groundwater extraction processes are:

- Pump-and-treat technology utilizes a submersible pump installed in a groundwater extraction well. The pump withdraws water to the surface to be treated before discharge.
- Dual-phase extraction technology combines soil vapor extraction with pump-and-treat technology.

These technologies are described in greater detail below.

**History.** Groundwater extraction is a remediation process which has been used for over 20 years in the LUFT industry.

### Pump-and-Treat

In a pump-and-treat system, contaminated groundwater or mobile NAPLs are captured in the saturated zone and pumped to the surface for treatment (EPA 1990). Pump-and-treat systems are used primarily to accomplish the following:

- **Hydraulic containment.** To control the movement of contaminated groundwater, preventing the continued expansion of the contaminated zone.
- **Treatment.** To reduce the dissolved contaminant concentrations in groundwater sufficiently that the aquifer complies with cleanup standards, or the treated water withdrawn from the aquifer can be put to beneficial use (EPA 1995).

### Advantages

- Proven performance, readily available equipment; easy installation.
- Minimal disturbance to site operations; can be used under buildings without excavation.
- Can be applied at sites with free product, and can be combined with other technologies.
- Can be used in unconfined aquifers.
- Resource can be treated and re-used.

### Disadvantages

- May require long operation time to achieve desired results.
- May not be effective in low-permeability soils.
- Large volume of extracted groundwater may require treatment.
- Requires complex monitoring and control during operation.

### Application

In order for pump-and-treat to be an effective remedial solution, the physico-chemical subsurface must allow contaminants to flow to the extraction wells. Consequently, the subsurface must have sufficient hydraulic conductivity (K) to allow fluid to flow readily and the chemicals must be transportable by the fluid (EPA 1990).

Cases in which contaminants cannot readily flow to pumping wells include:

- Heterogeneous aquifer conditions where low-permeability zones restrict contaminant flow toward extraction wells.
- Chemicals that are adsorbed or precipitated to the soil and slowly desorb or dissolve back into the groundwater as chemical equilibrium changes in response to the extraction process.

- Immobile NAPLs that may contribute to a miscible contaminant plume by prolonged dissolution (i.e., a separate-phase gasoline at residual saturation, EPA 1990).

In these cases, modifications to pump-and-treat technology, such as pulsed pumping, may be appropriate. Pump-and-treat may also be used in combination with other remedial alternatives, such as SVE and/or bioremediation.

The main limitation of pump-and-treat remediation is the long period of time that may be required to achieve an acceptable level of cleanup. The other issue with pump-and-treat technology at LUFT sites is that oily hydrocarbons can become trapped in the pore spaces by capillary forces and cannot readily be pumped out (EPA 1990).

Technologies which feature methods to address soils below the water table in combination with pump-and-treat systems can be more successful. Because oxygenates tend to have lower rates of adsorption, groundwater plumes composed primarily of oxygenates may respond well to simple groundwater extraction as a remediation process.

Further details regarding system design and operation and maintenance of pump-and-treat systems are available in EPA's 1990 publication entitled *Basics of Pump-and-Treat Ground-Water Remediation Technology* (EPA 1990).

## Dual-Phase Extraction

Dual-phase extraction (DPE), also known as multi-phase extraction, vacuum-enhanced extraction, or sometimes "bioslurping," is an *in-situ* technology that uses pumps to remove various combinations of contaminated groundwater, separate-phase petroleum product, and hydrocarbon vapor from the subsurface. Extracted liquids and vapor are treated and collected for disposal, or re-injected to the subsurface, where applicable (EPA 1994).

### Advantages

- Proven performance over a wide range of conditions. Requires no downhole pumps, but is flexible enough to allow their use if necessary.
- Minimal disturbance to site operations; can be used under buildings without excavation.
- Short treatment times (usually 6 months to 2 years under optimal conditions).
- Substantially increases groundwater extraction rates.
- Can be applied at sites with free product, and can be combined with other technologies.
- Can reduce the cost of groundwater treatment through air stripping within the vacuum-extraction tube.

### Disadvantages

- Single-pump systems are expensive to implement at sites with medium- to high-permeability soils; dual-pump systems may not be effective in low-permeability soils.
- Difficult to apply to sites where the water table fluctuates, unless water-table depression pumps are employed.
- Treatment may be expensive for extracted vapors and for oil-water separation.
- Large volume of extracted groundwater may require treatment.
- Requires specialized equipment with sophisticated control capability.
- Requires complex monitoring and control during operation.

### Application

DPE systems can be effective in removing separate-phase product (free product) from the subsurface, thereby reducing concentrations of petroleum hydrocarbons in both the saturated and unsaturated zones of the subsurface. DPE systems are typically designed to maximize extraction rates; however, the technology also stimulates biodegradation of petroleum constituents in the unsaturated zone by increasing the supply of oxygen.

DPE is often selected because it enhances groundwater and/or product recovery rates, especially in layered, fine-grained soils. The application of DPE also maximizes the effectiveness of SVE by lowering the water table and thereby increasing air-phase permeabilities in the vadose zone (EPA 1994).

### Operating Principles

The vacuum applied to the subsurface with DPE systems creates vapor-phase pressure gradients toward the vacuum well. These vapor-phase pressure gradients are also transmitted directly to the subsurface liquids present, and those liquids

existing in a continuous phase will flow toward the vacuum well in response to the imposed gradients. The higher the applied vacuum, the larger the hydraulic gradients that can be achieved in both vapor and liquid phases, and thus the greater the vapor- and liquid-recovery rates.

Dramatic enhancements in both water- and petroleum-product recovery rates resulting from the large hydraulic gradients attainable with DPE systems are possible. The depressed groundwater table that results from these high recovery rates serves both to hydraulically control groundwater migration and to increase the efficiency of vapor extraction. The remedial effectiveness of DPE within the zone of dewatering that commonly develops during DPE application should be greater than that of air sparging due to the more uniform air flow developed using DPE (EPA 1994).

Further details regarding system design and operation and maintenance of dual-phase extraction systems are available in EPA's 1994 publication entitled *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers* (EPA 1994).

# Remediation in the Saturated Zone:

## Natural Attenuation

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The American Society for Testing and Materials (ASTM) defines natural attenuation as “a potential remediation alternative for containment and reduction of the mass and concentration of petroleum hydrocarbons in the environment to protect human health and the environment. Remediation by natural attenuation depends upon natural processes such as biodegradation, dispersion, dilution, volatilization, hydrolysis, and sorption to attenuate petroleum constituents of concern to achieve remedial goals” (ASTM, E1943-98). Another important element of natural attenuation is that it occurs without human intervention.

Remediation by natural attenuation is usually used in conjunction with other remedial technologies or as a follow-up to active remediation to answer questions such as: 1) Is the plume stable? 2) Are concentrations of COCs decreasing? 3) What are the degradation rates? These questions are asked to determine whether natural attenuation will degrade COCs prior to the groundwater being used as a future beneficial resource.

Natural attenuation processes include a variety of physical, chemical, and biological processes that, under favorable conditions, reduce the mass, toxicity, mobility, volume, and/or concentration of contaminants in soil and/or groundwater. Processes that result only in reducing the concentration of a contaminant are termed “non-destructive” and include hydrodynamic dispersion, sorption, and volatilization. Other processes, such as biodegradation and abiotic degradation (e.g., hydrolysis), result in an actual reduction in the mass of contaminants and are termed “destructive” (EPA 1994). For petroleum hydrocarbons, biodegradation is the most important (and preferred) attenuation mechanism, since it is the only natural process that results in an actual reduction in the mass of petroleum hydrocarbons.

### Advantages of Natural Attenuation

In comparison to conventional engineered remediation technologies, natural attenuation offers a number of advantages, especially if intrinsic bioremediation is occurring:

- During intrinsic bioremediation, contaminants can ultimately be transformed to innocuous by-products (e.g., carbon dioxide and water in the case of fuel hydrocarbons), not just transferred to another phase or location within the environment.
- Natural attenuation is non-intrusive and allows continuing use of infrastructure during remediation.
- Natural attenuation does not involve generation or transfer of wastes.
- Natural attenuation is often less costly than other currently available remediation technologies.
- Natural attenuation can be used in conjunction with, or as a follow-up to, “intrusive” remediation measures.
- Natural attenuation is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime).

### Disadvantages of Natural Attenuation

Natural attenuation has the following potential disadvantages:

- Time frames for complete remediation may be long.
- Responsibility must be assumed for associated monitoring and its associated cost, and the implementation of institutional controls.
- Natural attenuation is subject to natural and anthropogenic changes in local hydrogeologic conditions, including changes in groundwater flow direction or velocity, electron acceptor and donor concentrations, and potential future releases.
- The hydrologic and geochemical conditions amenable to natural attenuation are likely to change over time and could result in renewed mobility of previously stabilized contaminants and may adversely impact remediation effectiveness.
- Aquifer heterogeneity may complicate site characterization, as it will with any remediation approach.

## Indicators and Parameters

Multiple distinct, but converging, lines of evidence are used to evaluate natural attenuation. The most common lines of evidence used to demonstrate natural attenuation of organic compounds dissolved in groundwater are historical trends, geochemical data, and microbiological data (as pioneered by the Air Force Center for Engineering and the Environment [AFCEE] in the 1990s).

Secondary parameters that are indicative of natural attenuation include, but are not limited to, pH, DO, ORP, sulfate, nitrate, Fe(II)/Fe(III) ratios, methane, and MTBE/TBA ratios. Additionally, aerobic bacterial population analysis (HPC) can be a useful indicator of indigenous microbial activity.

- **Historical trends.** The first line of evidence for natural attenuation is historical data that demonstrate a clear and meaningful trend of decreasing concentrations over time at appropriate monitoring points, which suggest a plume that is stable or retreating. A stable or retreating plume indicates that biodegradation is removing the mass of dissolved contaminants from the groundwater at a rate equal to or greater than the source is adding them to the plume. An increase in daughter-compound concentrations can also indicate biodegradation of the original compound: for example, decreases in the MTBE/TBA ratio as MTBE degrades to TBA.
- **Geochemical data.** A second line of evidence for natural attenuation involves geochemical indicators. Groundwater chemistry analytical data showing that geochemical conditions are suitable for biodegradation and that active biodegradation has occurred are indicated by: 1) Consumption/depletion of electron acceptors and donors, i.e., oxygen, nitrate, and sulfate 2) Production/increase of metabolic by-product concentrations, i.e., dissolved iron (II), manganese (II), and methane.

**Drilling Down.** Lower levels of oxygen, nitrate, and sulfate within a groundwater plume compared to upgradient or downgradient areas indicate that these parameters have decreased within the plume; they are evidence of biodegradation. Conversely, higher levels of methane, Fe(II), and manganese II within a plume compared to non-plume areas indicate that biodegradation is occurring within the plume area.

- **Dissolved oxygen (DO).** DO concentrations less than about 0.5 mg/L generally indicate that an anaerobic pathway exists. Field measurements made with electrodes are typically preferred over laboratory data. Samples should be protected from exposure to oxygen during sampling and analysis, as field measurement data reliability is a concern.
- **Microbiological data.** A third line of evidence for natural attenuation involves microbiological laboratory data (e.g., HPCs) or field data, which can be used to show that indigenous biota are capable of degrading site contaminants.

Typically, the use of electron acceptors is energetically favorable, meaning organisms able to use this compound for respiration will degrade waste compounds the most rapidly. The inventory below lists compounds in order of energetic favorability.

- 1) Aerobic respiration (oxygen use)
- 2) Denitrification (nitrate used as substrate)
- 3) Manganese (IV) reduction
- 4) Ferric iron (Fe[III]) reduction
- 5) Sulfate reduction
- 6) Methanogenesis

Table 16 describes various analytes likely to be present in samples collected at LUFT sites and the trends in analyte concentrations that will be visible if biodegradation is occurring.



**Table 16 – Trends in Contaminant, Electron Acceptor, and Metabolic By-Product Concentrations during Biodegradation**

Analyte	Trend in Analyte Concentration During Biodegradation	Terminal Electron Accepting Processes Causing Trend
Petroleum hydrocarbons	Decreases	Aerobic Respiration, Denitrification, Manganese (IV) Reduction, Fe(III) Reduction, Sulfate Reduction, Methanogenesis
Dissolved Oxygen (DO)	Decreases	Aerobic Respiration
Nitrate	Decreases	Denitrification
Manganese (II)	Increases	Manganese (IV) Reduction
Fe(II)	Increases	Fe(III) Reduction
Sulfate	Decreases	Sulfate Reduction
Methane	Increases	Methanogenesis
Chloride	Increases	Reductive Dechlorination or Direct Oxidation of Chlorinated Compound
Oxidation-Reduction Potential (ORP)	Decreases	Aerobic Respiration, Denitrification, Reduction, Fe(III) Reduction, Sulfate Reduction, Methanogenesis, and Halorespiration
Alkalinity	Increases	Aerobic Respiration, Denitrification, Fe(III) Reduction, and Sulfate Reduction

## Data Collection

The indicators and parameters of natural attenuation are monitored for a period of time and the duration of monitoring is specific to each LUFT site. Historically, there has been a belief that natural attenuation requires a long-term monitoring program. Current practical data suggest that, if trends are shown consistently over the course of a year accounting for fluctuations in groundwater elevations, long-term monitoring is not necessary.

Data collection for natural attenuation may not be needed at all of the monitoring well locations at a LUFT site. With the approval of the agency case worker, the select wells and/or specific frequencies can be determined such that the level of data collected is accurate to demonstrate the decreasing trends of COCs, plume stability, etc. Most importantly, monitoring should be conducted only until it has been demonstrated that natural attenuation will continue and eventually meet remedial goals, prior to the resource being needed for a beneficial use, and not for extended periods of time beyond what is needed to establish a data trend.

**Further Reading.**

This text is an excerpt from the following website:

<http://www.afcee.af.mil/resources/technologytransfer/programsandinitiatives/monitorednaturalattenuation/long-termmonitoring/index.asp>

# Remediation

## Remedial Effectiveness



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After a remedial technology is installed and operational, it is important to determine whether that technology is effective. Generally, declining trends in extracted vapor and/or groundwater are evidence of success.

Declining groundwater concentrations of COCs as compared with data collected before the onset of remediation are evidence of success. Evidence of ineffectiveness includes groundwater concentrations of COCs that persist at or near levels observed before the start of cleanup. Increases in concentrations in wells downgradient from the treatment area may indicate a detrimental effect; for example, incomplete oxidation during ozone sparging. In such cases, the process is promptly stopped to examine potential problems and plan further action.

Exceptions to this generalization include temporary increases in groundwater concentrations in the treatment area shortly after initiation of some forms of remediation. These can be a sign of successful implementation. For example, increases in dissolved-gasoline concentrations after initiation of air sparging in the source area usually represent COCs being stripped from soils below the water table by the sparging process, followed by dissolution in the groundwater. Continued sparging should result in decreasing concentrations over time following the initial "spike" in levels. This effect is also seen during enhanced bioremediation, due to surfactants produced by the microbes as a by-product of metabolism.

For many of these assessments, readily available geographical information systems (GIS) software and simple trend-analysis statistical tools are very useful for data visualization and performance assessment; such tools can enhance data-analysis capabilities.

**Further Reading.** Information from this chapter and further information are available from "Evaluating Remedial Performance" (from *Remediation Process Optimization: Identifying Opportunities for Enhanced and More Efficient Site Remediation*, 2004, prepared by The Interstate Technology & Regulatory Council [ITRC] Remediation Process Optimization Team).

One of the challenges of effective remediation is determining when remediation is complete. If the RP, in partnership with his/her consultant, does not efficiently manage the endpoint of the remediation process, the lack of operation limits (shutdown criteria) can result in significant unnecessary costs to both the RP and the UST Cleanup Fund.

In general, once extracted media (vapors, groundwater) or dissolved-plume concentrations decline to stable minimum levels (the third, diffusional stage of extraction), the effective performance limit of the remediation process has been reached. Once it is clear that the remediation system has reached this performance limit, the site's path forward is revisited with the lead agency.

If the remediation system performance limit is reached and concentrations remain above remediation goals after verification testing, potential options to be discussed with the regulatory case worker may include

- Installation of a new remediation system with different performance goals,
- Risk modeling of remaining concentrations in lieu of further physical treatment, and/or
- Deed restrictions, if approved by the property owner.

If reaching equipment performance limits, however, coincides with concentration declines in soil and/or groundwater to defined goals, then remediation is by definition fully complete.

# Remediation

## References



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- Ahn, M. 2003. Remediation of Chromium(VI) in the Vadose Zone: Stoichiometry and Kinetics of Chromium(VI) Reduction by Sulfur Dioxide. August.
- Alabama State Water Program. On-Line Dictionary. "Groundwater Mounding." Definition available at: [http://www.aces.edu/waterquality/glossary/glossary\\_results.php3?rowid=2228](http://www.aces.edu/waterquality/glossary/glossary_results.php3?rowid=2228). Accessed on 1/14/10.
- American Society for Testing and Materials (ASTM). 2004. Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites. ASTM E1943-98.
- DiGiulio, D. 1992. Evaluation of Soil Venting Application. Ada, OK: U.S. Environmental Protection Agency, Office of Research and Development. EPA/540/S-92/004.
- Interstate Technology & Regulatory Council (ITRC). 2009. *Evaluating LNAPL Remedial Technologies for Achieving Project Goals*. December.
- Johnson, P.C., Stanley, C.C., Kemblowski, M.W., Byers, D.L., and J.D. Colthart. 1990. A Practical Approach to the Design, Operation and Monitoring of *In-Situ* Soil-Venting Systems. *Ground Water Monitoring Review*, Vol. 10, No. 2, pp. 159-178.
- Johnson, R.L., P.C. Johnson, D.B. McWhorter, R.E. Hinchee, and I. Goodman. 1993. An overview of *in-situ* air sparging. *Ground Water Monitoring Review*. Vol. 13, No. 4, pp. 127-135.
- Kinsella, J.V. and M.J.K. Nelson. 1993. *In-Situ* Bioremediation: Site Characterization, System Design and Full-Scale Field Remediation of Petroleum Hydrocarbon- and Trichloroethylene-Contaminated Groundwater in P.E. Flathman and D.E. Jerger, eds., *Bioremediation Field Experience*. Boca Raton, FL: CRC Press.
- Marley, M., D.J. Hazenbronck, and M.T. Walsh. 1992. The application of *in-situ* air sparging as an innovative soils and groundwater remediation technology. *Ground Water Monitoring Review*. Vol. 12, No. 2, pp. 137-145.
- Martin, L.M., R.J. Sarnelli, and M.T. Walsh. 1992. Pilot-scale evaluation of groundwater air sparging: site-specific advantages and limitations, in Proceedings of R&D 92-National Research and Development Conference on the Control of Hazardous Materials. Greenbelt, MD: Hazardous Materials Control Research Institute.
- Norris, R.D. 1994. *In-Situ* Bioremediation of Soils and Groundwater Contaminated with Petroleum Hydrocarbons in R.D. Norris, R.E. Hinchee, R.A. Brown, P.L. McCarty, L. Semprini, J.T. Wilson, D.H. Kampbell, M. Reinhard, E.J. Bower, and R.C. Borden. *Handbook of Bioremediation*. Boca Raton, FL: CRC Press.
- Norris, R.D. and K.D. Dowd. 1993. *In-Situ* Bioremediation of Petroleum Hydrocarbon-Contaminated Soil and Groundwater in a Low-Permeability Aquifer in P.E. Flathman and D.E. Jerger, eds., *Bioremediation Field Experience*. Boca Raton, FL: CRC Press.
- Norris, R.D., Hinchee, R.E., Brown, R.A., McCarty, P.L., Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bower, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and C.H. Ward. 1993. *In-Situ* Bioremediation of Ground Water and Geological Material: A Review of Technologies. Ada, OK: U.S. Environmental Protection Agency, Office of Research and Development. EPA/5R-93/124. (NTIS: PB93-215564/XAB).
- Norris, R.D., Hinchee, R.E., Brown, R.A., McCarty, P.L., Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bower, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and C.H. Ward. 1994. *Handbook of Bioremediation*. Boca Raton, FL: CRC Press.
- Nyer, E.K. 1993. Practical Techniques for Groundwater and Soil Remediation. Boca Raton, FL: Lewis Publishers, CRC Press, Inc.
- Riser-Roberts, E. 1992. Bioremediation of Petroleum Contaminated Sites. NCEL, Port Hueneme, CA: C. K. Smoley Publishers, CRC Press.

- Sims, J.L., J.M. Suflita, and H.H. Russell. 1992. *In-Situ* Bioremediation of Contaminated Groundwater. Washington, DC: U.S. Environmental Protection Agency, EPA/540/S-92/003, (NTIS: PB92-224336/XAB). February.
- Staps, S.J.J.M. 1990. International Evaluation of *In-Situ* Bioremediation of Contaminated Soil and Groundwater. Washington, DC: U.S. Environmental Protection Agency, Office of Emergency and Remedial Response. EPA 540/2-90/012.
- Schwartz, O.R., J.A. Berndt, and J.A. Mundell. 2005. The Use of Ozone Sparging to Remove MTBE from Groundwater in Uniform Sand Aquifer. Proceeding of the 2005 National Groundwater Association Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy. San Francisco, CA. pp. 150-162.
- U.S. Environmental Protection Agency (USEPA). 1990. Basics of Pump-and-Treat Ground-Water Remediation Technology. Environmental Research Laboratory. EPA/600/8-90/003.
- USEPA. 1991a. Soil Vapor Extraction Technology: Reference Handbook. Cincinnati, OH: Office of Research and Development. EPA/540/2-91/003.
- USEPA. 1991b. Guide for Treatability Studies under CERCLA: Soil Vapor Extraction. Washington, DC: Office of Emergency and Remedial Response. EPA/540/2-91/019A.
- USEPA. 1991c. Guide for Conducting Treatability Studies under CERCLA: Aerobic Biodegradation Remedy Screening. Washington, DC: Office of Emergency and Remedial Response. EPA/540/2-91/013A.
- USEPA. 1992. A Technology Assessment of Soil Vapor Extraction and Air Sparging. Washington, D.C. Office of Research and Development. EPA/600/R-92/173.
- USEPA. 1993. HyperVentilate. A Software Guidance System Created for Vapor Extraction Systems for Apple Macintosh and IBM PC-Compatible Computers. EPA 510-F-93-001.
- USEPA. 1994. How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers (Chapter VII). (EPA 510-B-95-007). October. Available at <http://www.epa.gov/OUST/pubs/tums.htm>. Accessed on 1/14/10.
- USEPA. 1995. Pump-and-Treat Ground-water Remediation. A Guide for Decision Makers and Practitioners. Office of Research and Development, Washington D.C. 20460. EPA/625/R-95/005. July.

**CA LUFT MANUAL**  
**SECTION 4**  
**GLOSSARY and ACROYNMS**

# Glossary

Version 1.0 - Draft August 2010



## Scope of This Chapter

This Glossary provides the definitions of terms used in this Manual.

Many terms in this Glossary are ordinary words used in daily life ("gasoline"); others are "terms of art" (i.e., specific to this kind of work) and may be used differently in LUFT contexts as opposed to other contexts. If there is any doubt about the meaning of a term found in the CA LUFT Manual, please look for it here. If the term in question isn't in the Glossary, it's most likely

- a professionally defined, specific, non-ambiguous term (e.g., well boring logs, Unified Soil Classification System) or
- a chemical compound or group of compounds whose specific structure or behavior is best illustrated, described, and/or modeled on the Internet or in a chemistry textbook

Any terms which refer to trade-marked or registered product names are understood to include the <sup>TM</sup> or <sup>®</sup> mark throughout this CA LUFT Manual, even if not printed at each mention of the product name.

Entries in this Glossary are presented in alphabetical order and have been **shown in this font** whenever they appear under the definition of another term. **Boldface** and *italics* have been used here for their normal purposes. When an entry in this Glossary is also known by another name, that secondary name is shown in SMALL CAPITAL LETTERS under the primary definition (for an example, see **Alkanes**).

### Abandoned well

- A groundwater well used less than 8 hours in any 12-month period.
- A monitoring well from which no monitoring data have been collected for a period of 2 years.
- A well which is in such a state of disrepair that it cannot be made functional for its original use or for any other use regulated by this Manual.
- An engineering test hole after 24 hours or more have elapsed since the construction and testing work at the site were completed.

### Advection

Advection is the transport of dissolved constituents with groundwater and is, therefore, dependent on the **hydraulic conductivity** of the subsurface materials and hydraulic gradient in the aquifer. From the [Fate and Transport](#) chapter.

### Aerobic biodegradation

The breakdown of organic contaminants by microorganisms when oxygen is present. Aerobic bacteria use oxygen as an electron acceptor, and break down organic chemicals into smaller organic compounds, often producing carbon dioxide and water as the final products. Aerobic biodegradation is also known as AEROBIC RESPIRATION. Aerobic biodegradation is an important component of the natural attenuation of contaminants at many hazardous-waste sites.

From [http://toxics.usgs.gov/definitions/aerobic\\_biodegradation.html](http://toxics.usgs.gov/definitions/aerobic_biodegradation.html)

### Air toxics

Chemicals released into the air that are known or suspected to cause cancer, or other serious health problems, such as birth defects or reproductive effects. Vehicle exhaust contains substantial amounts of air toxics. The California Air Resources Board (CARB) has identified diesel exhaust particulate as the #1 air-borne carcinogen in the state.

From <http://www.sbcapcd.org/sbc/pollut.htm> (Santa Barbara County Air Pollution Control District)

### Alcohols

Any of a series of *hydroxyl compounds*, the simplest of which are derived from saturated hydrocarbons and have the general formula  $C_nH_{2n+1}OH$ , including methanol ( $CH_3OH$ ) and ethanol ( $C_2H_5OH$ ). (*Hydroxyl compounds* contain an oxygen atom and a hydrogen atom bonded covalently to one another.)



## Aliphatic compounds

Of, relating to, or designating a group of organic chemical compounds in which the carbon atoms are linked in open chains or in ring compounds without double bonds (**vs. aromatics**, where the carbon atoms are arranged in ring structures that have double bonds in them). The carbon atoms can be joined by single, double, or triple bonds. Examples of aliphatic compounds are shown in the chapter on [Fate and Transport](#).

## Alkanes

Alkanes are chemical compounds consisting only of the elements carbon (C) and hydrogen (H) (i.e., hydrocarbons), in which these atoms are linked together exclusively by single bonds (i.e., they are saturated compounds) without any cyclic structure or “loops.” The alkanes form a group of saturated, open-chain hydrocarbons having the general formula  $C_nH_{2n+2}$ —for example,  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , etc.

## Alkenes

Alkenes are unsaturated chemical compounds containing at least one C-C double bond. The simplest non-cyclic alkenes, with only one double bond and no other functional groups, form a homologous series of hydrocarbons with the general formula  $C_nH_{2n}$  (for example, ethylene gas,  $C_2H_4$ ).

## Alkyl groups

Alkyl groups are hydrocarbons (C + H); typically an alkyl group is a part of a larger molecule. The term is usually used loosely; there is no general formula for an alkyl group. In structural formulae, an alkyl group is represented with an “R.” Usually, alkyl groups resemble hydrocarbons, but with one less hydrogen atom. The smallest alkyl group is a methyl ( $CH_3$ ).

## Anaerobic biodegradation

The breakdown of organic contaminants by micro-organisms when oxygen is not present. Some anaerobic bacteria use nitrate, sulfate, iron, manganese, or carbon dioxide as their electron acceptors, and break down organic chemicals into smaller compounds, often producing carbon dioxide and methane as the final products. This general mechanism of anaerobic biodegradation is an example of *anaerobic respiration*. Alternatively, some anaerobic microorganisms can break down organic contaminants by *fermentation*. *Fermentation* takes place when the organic chemical acts as an electron acceptor. Anaerobic biodegradation is an important component of the natural attenuation of contaminants at many hazardous-waste sites.

From [http://toxics.usgs.gov/definitions/anaerobic\\_biodegradation.html](http://toxics.usgs.gov/definitions/anaerobic_biodegradation.html)

## Analyte(s)

Compound(s) for which an analytical laboratory has been requested to analyze a given sample or set of samples.

## Anoxic

An adjective that means “without oxygen.” For example, anoxic groundwater contains no dissolved oxygen. Anoxic groundwater conditions at hazardous-waste sites are common because biodegradation processes often use up all the available oxygen. A related term is **anaerobic**.

From <http://toxics.usgs.gov/definitions/anoxic.html>

## Anthropogenic

Caused by human beings as opposed to the processes of nature.

## Aquiclude

A body of rock that will absorb water slowly but will not transmit it fast enough to supply a well or spring.

From *Dictionary of Geological Terms*.

## Aquifer

An aquifer is an underground layer of water-bearing permeable rock or unconsolidated materials (gravel, sand, silt, or clay) from which groundwater can be usefully extracted using a water well. An aquifer provides groundwater for drinking, irrigation, and other beneficial uses. In California, the protection of groundwater quality in aquifers (and other bodies of fresh water) is within the purview of the State Water Resources Control Board (SWRCB).

## Aquitard

A body of impermeable or distinctly less permeable material stratigraphically adjacent to one or more **aquifers** which retards but does not prevent the flow of water to or from an adjacent **aquifer**. An aquitard does not readily yield water to wells or springs, but may serve as a storage unit for groundwater.

## Aromatic compounds

Hydrocarbons, compounds composed of carbon and hydrogen, are divided into two classes: aromatic compounds, which contain one or more aromatic rings (i.e. a ring with double bonds, such as benzene), and **aliphatic compounds**, which do not contain aromatic rings (see the [Fate and Transport](#) chapter).

## Benzene, toluene, ethylbenzene, and xylenes (BTEX)

Benzene, toluene, ethylbenzene, and xylenes (“BTEX”) are four **volatile organic compounds (VOCs)** found in gasoline. They are mobile in the subsurface and in the atmosphere, and of concern for underground storage tank (UST) remediation sites due to their mobility and toxicity. Because they are found together and are similar in their chemical properties, they’re often referred to by the acronym BTEX (BEE-TEX).

## Best Management Practices (BMPs)

Practical and effective measures to protect natural resources. Historically, the term has referred to pollution controls in the fields of industrial wastewater control and municipal sewage control, while in stormwater management (both urban and rural) and wetland management.

## Biodegradation

Biodegradation is the breakdown of organic contaminants into smaller compounds by microbial organisms. The microbial organisms transform the contaminants through metabolic or enzymatic processes. Biodegradation processes vary greatly, but frequently the final product of the degradation is carbon dioxide or methane. Biodegradation is a key process in the natural attenuation of contaminants at LUFT sites.

From <http://toxics.usgs.gov/definitions/biodegradation.html>

## Capillary fringe

The capillary fringe is mostly saturated (or completely saturated) zone just above the water table in which groundwater is drawn up from a water table by capillary action. Water content decreases with distance above the water table. Pores at the base of the capillary fringe are fully saturated due to tension saturation. If pore size is small and relatively uniform, it is possible that soils can be completely saturated with water for several feet above the water table. Alternately, the saturated portion will extend only a few inches above the water table when pore size is large.

See the [Fate and Transport](#) chapter for an illustration.

## centiPoise (cP)

The unit used to express dynamic viscosity. Water at 20 °C has a viscosity of 1.0020 cP, or 0.001002 kilogram/meter second.

$$1 \text{ P} = 1 \text{ g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$$

More at <http://en.wikipedia.org/wiki/Viscosity>

## Co-metabolic, co-metabolism

When two or more **microorganisms** are required for the **biodegradation** of petroleum hydrocarbons, they are said to be co-metabolizing the target hydrocarbon(s). Some compounds that are resistant to standard monocultural **biodegradation** (by a given species of bacterium, for example) have proved to be biodegradable with combinations of two, three, or more different species.

## Confined aquifer

An **aquifer** separated from the ground surface or from an overlying aquifer by an **aquiclude** or an **aquitard** (usually a layer of non-porous clay-type soil) to the extent that pressure can be created in the lower reaches of the **aquifer** without affecting either the soil surface or the upper reservoir of water.

## Consultant

The consultant is defined as a third party (not the RP and not a regulator), generally a licensed and experienced professional geologist or environmental engineer, hired by a responsible party to perform tasks associated with the investigation and remediation of a LUFT site.

## Constituent(s) of concern (COCs)

Contaminants in environmental media that may cause a risk to human health, safety, or the environment that have been identified for further evaluation, such as a risk assessment.

## Cyclic alkanes

Cycloalkanes (also called NAPHTHENES, especially if from petroleum sources) have one or more rings of carbon atoms in their chemical structure. Like **alkanes**, cycloalkanes consist of only carbon (C) and hydrogen (H) atoms and are saturated; there are no double or triple C-C bonds. The general chemical formula for cycloalkanes is  $C_nH_{2(n+1-g)}$ , where  $g$  = the number of rings in the molecule. A cycloalkane with a single ring is named in parallel with its non-cyclic **alkane** counterpart possessing the same number of carbon atoms: cyclopropane ( $C_3H_6$ ) **vs.** propane ( $C_3H_8$ ), cyclobutane ( $C_4H_8$ ) **vs.** butane ( $C_4H_{10}$ ), etc.

## Data Quality Objectives (DQOs)

DQOs are qualitative and quantitative statements specified to ensure that data of known and appropriate quality are obtained. The DQO process is a series of planning steps, typically conducted during site assessment and investigation, that is designed to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate. The DQO process involves a logical, step-by-step procedure for determining which of the complex issues affecting a site are the most relevant to planning a site investigation before any data are collected.

From <http://www.brownfieldstsc.org/glossary.cfm?lett=D>

## Destroy

To fill a well completely, usually with concrete (including both interior and annular spaces, if the well is cased), so that it will not produce water or act as a conduit for the transmission of water between any water-bearing formations penetrated.

## Detection Limits

**DETECTION LIMIT** – the lowest amount that can be distinguished from the normal “noise” of an analytical instrument or methods.

**INSTRUMENT DETECTION LIMIT** – the lowest amount of a substance that can be detected by an instrument without correction for the effects of sample matrix, handling, and preparation.

**METHOD DETECTION LIMIT** – the detection limit that takes into account the reagents, sample matrix, and preparation steps applied to a sample in specific analytical methods.

**SAMPLE QUANTITATION LIMIT** – a quantitation limit that accounts for sample characteristics, sample preparation, and analytical adjustments, such as dilution.

The above four terms from:

<http://www.deq.virginia.gov/vrprisk/glossary.html> .

**REPORTING LIMIT** – The lowest concentration at which a contaminant is reported.

From <http://www.uldrinkwell.com/drinkwell/glossary.html> .

## Diesel, “middle-weight” hydrocarbons

Diesel fuel #2 (also fuel oil #2) is composed primarily of C10 to C25 hydrocarbons, including **aliphatics**, minor amounts of monoaromatics, and **Poly Aromatic Hydrocarbons (PAHs)** (EPA 1996). Diesel fuel and fuel oils are much less chemically complex than gasoline, and their components have not changed very much throughout manufactured history. Besides diesel, other middle-distillate fuels include:

- Kerosene (approximately C8 to C18),
- Kerosene-based jet fuels [e.g., Jet A or JP-5 (C8 to C18) or JP-8 (C8 to C20)],
- Diesel fuel #1 or fuel oil #1 (approximately C8 to C22), and
- Heavier fuel oils such as marine diesel or diesel/ fuel oil #4 (approximately C12 to C30).

See the [Fate and Transport](#) chapter.

## Dipping strata

Non-horizontal sediments or layers of bedrock/ formation whose inclination from the horizontal affects the migration of subsurface substances.

## Dispersion

Dispersion is the spread of dissolved constituents predominantly in the direction of groundwater flow, but also in directions other than would be expected due to groundwater movement only (lateral and vertical). Dispersion causes some attenuation of the concentrations (lower concentrations) as the constituent moves downgradient.

From the [Fate and Transport](#) chapter.

## Effective Solubility

The maximum dissolved-phase concentration when a compound is part of a chemical mixture. This is always less than the chemical's pure-phase solubility in water. The effective solubility is calculated from the compound's mole fraction in the mixture and the chemical's pure phase solubility in water.

## Ex-situ

Away from its native location, moved from its original place; excavated; removed or recovered from the subsurface.

From [http://www.epa.gov/OUST/pubs/tum\\_appx.pdf](http://www.epa.gov/OUST/pubs/tum_appx.pdf).

## Fractionate

To separate a chemical compound into components; for example, by distillation or crystallization.

## Gasoline

Gasoline is typically composed of C4 to C12 hydrocarbons, with the majority of the mass between C4 and C10. These lighter-weight hydrocarbons include **aliphatics** and **aromatics** (including **BTEX**). Minor amounts of the smallest **PAHs**, naphthalene and methylnaphthalenes, are also usually present. The proportion of various hydrocarbons is variable and is a function of the refining process and performance specifications.

## Greenhouse gas

Without the "greenhouse effect," Earth would be too cold—an estimated 30 °C (54 °F) less than current average temperatures—for life to survive. Our atmosphere, and its effective trapping of solar heat, enables plants and animals, including people, to eat and live. There are six greenhouse gases active in the planetary greenhouse effect; three of them are naturally occurring but can also be generated by human activity, and three of them are generated solely by human activity.

Naturally Occurring Gases:

- Carbon dioxide (CO<sub>2</sub>)
- Methane (CH<sub>4</sub>)
- Nitrous oxide (N<sub>2</sub>O)

Industrial Gases:

- Hydrofluorocarbons (HFCs)
- Perfluorocarbons (PFCs)
- Sulfur hexafluoride (SF<sub>6</sub>)

For more information, or to see an illustration of the natural greenhouse effect, go to:

[http://tonto.eia.doe.gov/energyexplained/index.cfm?page=environment\\_about\\_ghg](http://tonto.eia.doe.gov/energyexplained/index.cfm?page=environment_about_ghg)

## Groundwater Basin

A groundwater reservoir defined by the overlying land surface and the underlying aquifers that contain water stored in the reservoir. Boundaries of successively deeper aquifers may differ and make it difficult to define the limits of the basin. (Municipal Water District of Orange County <http://www.mwdoc.com/glossary.htm> )

## Heavy fuel oils (lubricating oils and hydraulic oils)

Heavy fuel oils and lubricants are very similar to **middle distillate fuels, such as diesel**, in their composition and characteristics, except that the predominant compounds have higher molecular weights. These fuels are viscous and

insoluble, and thus highly immobile in the subsurface. Lubricating oils are composed primarily of C25 to C32 hydrocarbons, which are almost exclusively **aliphatics** (branched and cyclic **alkanes**). **Aromatic** hydrocarbons are not present in lubricating oils prior to use in engines. Because of their very large molecular sizes and the fact that they are exclusively **aliphatic**, lubricating oils are nearly insoluble in groundwater, are not volatile, and pose virtually no risk to human health. From the [Fate and Transport](#) chapter.

### Henry's Law Coefficient (or Constant)

This is the ratio of the vapor-phase concentration of an organic chemical relative to its dissolved phase concentration in water. See **vapor pressure**.

### Hydraulic conductivity (of soils)

Hydraulic conductivity is a quantitative measure of a saturated soil's ability to transmit water when subjected to a hydraulic gradient. It can be thought of as the ease with which pores of a saturated soil permit water movement.

Based on <http://soils.usda.gov/technical/technotes/note6.html>

### Hydrogeology

Hydrogeology (also known as GEOHYDROLOGY) is a branch of hydrology which relates to groundwater, subsurface, or subterranean water. Hydrogeology involves the study of the distribution and movement of water below the Earth's surface, especially the distribution of aquifers, groundwater flow, and groundwater quality.

From

<http://www.water-technology.net/glossary/hydrogeology.html>

### Hydrology

Hydrology is the science that encompasses the occurrence, distribution, movement, and properties of the waters of the earth (both surface and subsurface water bodies) and their relationship with the environment within each phase of the hydrologic cycle, also referred to as the WATER CYCLE.

From <http://ga.water.usgs.gov/edu/hydrology.html>

### In-situ

In its original place; unmoved; unexcavated; remaining in the subsurface.

From [http://www.epa.gov/OUST/pubs/tum\\_appx.pdf](http://www.epa.gov/OUST/pubs/tum_appx.pdf)

### Light non-aqueous-phase liquid (LNAPL), DNAPL

LNAPL is "pure product" (e.g., gasoline) that remains undiluted as the original bulk liquid in the subsurface. When petroleum is released into the environment, it is typically released as a light non-aqueous-phase liquid (LNAPL). LNAPLs (including gasoline, diesel, and other fuels, most crude oils, and creosote) are less dense than water, while *dense* non-aqueous phase liquids (such as many chlorinated solvents) are more dense than water. This Manual discusses LNAPLs only, as these are petroleum-hydrocarbon based.

### Lower Explosive Limit (LEL)

The Flammable Range (Explosive Range) is the range of a concentration of a gas or vapor that will burn (or explode) if an ignition source is introduced.

Below the explosive or flammable range, the mixture is too lean to burn; above the upper explosive or flammable limit, the mixture is too rich to burn. The limits are commonly called the "Lower Explosive or Flammable Limit" (LEL/LFL) and the "Upper Explosive or Flammable Limit" (UEL/UFL).

From [http://www.engineeringtoolbox.com/explosive-concentration-limits-d\\_423.html](http://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html),

which also provides a table of LELs and UELs for many common gases, expressed as a percent gas.

### Mass spectrometry

Mass spectrometry (MS) is an analytical technique for the determination of the elemental composition of a sample or molecule. It is also used for elucidating the chemical structures of molecules. The MS principle consists of ionizing chemical compounds to generate charged molecules or molecule fragments and measurement of their mass-to-charge ratios. In a typical MS procedure:

- 1) a sample is loaded onto the MS instrument, and undergoes vaporization,

- 2) the components of the sample are ionized by one of a variety of methods (e.g., by impacting them with an electron beam), which results in the formation of positively charged particles (ions),
- 3) the positive ions are then accelerated by an electric field,
- 4) computation of the mass-to-charge ratio ( $m/z$ ) of the particles based on the details of motion of the ions as they transit through electromagnetic fields, and
- 5) detection of the ions, which in step 4 were sorted according to  $m/z$ .

More detail on steps 4 and 5: The streams of sorted ions pass from the analyzer to the detector, which records the relative abundance of each ion type. This information is used to determine the chemical element composition of the original sample.

From [http://en.wikipedia.org/wiki/Mass\\_spectrometry](http://en.wikipedia.org/wiki/Mass_spectrometry)

### Maximum Contaminant Levels (MCLs)

Maximum Contaminant Levels (MCLs) are maximum concentration levels allowed by law in public water supplies promulgated by the State of California Department of Public Health and published in Titles 17 and 22 of the *California Code of Regulations*.

### Methanogenesis, methanogenic

The fermentation by **microorganisms** of simple organic carbon compounds or oxidation of  $H_2$  under **anaerobic** (without oxygen) conditions with the production of  $CH_4$  and  $CO_2$ . Methanogenic conditions prevail in many contamination plumes after all other electron acceptors ( $O_2$ ,  $NO_3$ ,  $Fe^{+3}$ , and  $SO_4$ ) have been used up by other members of the subsurface microbial community.

From <http://toxics.usgs.gov/definitions/methanogenesis.html>

### Microorganisms

Soil normally contains large numbers of diverse microorganisms, including bacteria, algae, fungi, protozoa, and actinomycetes. Many of these microorganisms assist in the processes of **natural attenuation** and/or **biodegradation**.

### Middle-weight hydrocarbons, middle distillate fuels

See **Diesel**

### Mole-fraction

The **mole fraction** is the number of moles of a given compound divided by the total number of moles of all compounds in the given solution or gas. The mole fraction is used to estimate the compound's effective solubility (maximum dissolved-phase concentration) or maximum vapor-phase concentration.

The mole fraction of compound  $i$  in a TPH mixture (such as LNAPL),  $x$ , is calculated from

$$x = \frac{C_i \cdot MW_{TPH}}{MW_i \cdot C_{TPH}}$$

where

$MW_{TPH}$  = average molecular weight of the hydrocarbon mixture (or product) [g/mol]

$MW_i$  = molecular weight of component  $i$  [g/mol]

$C_{TPH}$  = TPH concentration (usually measured in as total concentration in soil) [g/g]

$C_i$  = concentration of component  $i$  in the mixture (usually measured as total concentration in soil) [g/g]

### Natural attenuation

Natural-attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, and/or concentration of contaminants in soil or groundwater. These processes include **biodegradation**, dispersion, dilution, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants.

From <http://www.epa.gov/oust/directiv/d9200417.pdf>

### Monitoring well

A well constructed exclusively to monitor and/or sample conditions of a water-bearing **aquifer**, e.g., water pressure, depth, movement, temperature, or quality.

## Non-detectable concentrations(s)

Chemicals that are not detected in a sample above a certain limit, usually the quantitation limit for the chemical in the sample. See **Detection Limits**.

## Organoleptic

Of or pertaining to the sensory properties of a chemical, such as taste and odor. For example, the California MCL for MTBE is based on organoleptic properties rather than its toxicity.

## Over-excavation

Over-excavation is any additional excavation needed after a UST and the surrounding soil have been removed. Confirmation samples are usually collected from the walls and floor of the excavation pit and sent for laboratory analysis to ensure that the remaining soil does not present a threat to groundwater. However, if the analytical results of the soil samples reveal unexpectedly high concentrations of targeted analytes, or perhaps the presence of unexpected analytes, over-excavation may be appropriate.

## Oxidation/reduction (“redox”) reaction

Redox reactions (the common name for oxidation-reduction reactions) generate the energy required in order for biodegradation to occur; they are fundamentally a set of reactions explaining the transfer of electrons between compounds. *Oxidation* is the half-reaction involving the loss of electrons, and *reduction* is the half-reaction involving the gain of electrons. These reactions are always paired—oxidation and reduction happen virtually simultaneously.

In the context of **biodegradation**, the important thing to remember about redox reactions is that these reactions are needed to release energy to be used for microbial growth. The more energy derived from a redox reaction, the faster **microorganisms** utilizing that reaction can grow.

From the [Fate and Transport](#) chapter.

## Oxygenate

Oxygenates are fuel additives (alcohols and ethers) that contain oxygen, which can boost gasoline’s octane quality, enhance combustion, and reduce exhaust emissions. In California, the term “oxygenated gasoline” most commonly refers to the type of gas sold during wintertime in order to reduce emissions of carbon monoxide (CO) from motor vehicles.

From <http://www.epa.gov/OMS/oxygenate.htm> ).

## Physico-chemical properties

This is a short-hand phrase used to refer to the physical and chemical properties of a given chemical or compound. Physico-chemical properties can include, but aren’t limited to, aqueous solubility, vapor pressure, density, the Henry’s Law constant, specific gravity, and biodegradability. These properties are needed to evaluate the fate and transport of the chemical.

## Plan-view site map

Plan view is sometimes also referred to as BIRD’S-EYE VIEW. A site map in plan view shows all current and salient former features of the site.

## Polycyclic aromatic hydrocarbons (PAHs)

PAHs are chemical compounds that consist of fused **aromatic** rings. They are of concern because some compounds have been identified as carcinogenic, mutagenic, and/or teratogenic and therefore have high toxicity values.

## Owner, operator

“Owner” is defined in the California Health and Safety Code as the owner of an UST; “operator” is defined as any person in control of, or having daily responsibility for, the daily operation of a UST. The owner/operator is usually the responsible party (RP) at a LUFT site.

From California H&SC §25281.



## Receptor

A receptor is a human or other living organism with the potential to be exposed to and adversely affected by contaminants because it is present at the source or along the contaminant migration pathway.  
From the [Conceptual Site Model](#) chapter.

## Responsible party (RP)

The party (or parties) responsible for the LUFT site. Usually the RP is the site owner or operator. (See **Owner, operator**.) Sometimes the RP(s) can include former owners of the site or the party supplying the fuel.

## Saturated zone

The subsurface zone in which all the voids (spaces between particles of rock/soil) in the rock or soil are filled with water. The water table is the top of the saturated zone in an unconfined **aquifer**.

## Smear zone

The smear zone is the area where free product, which settled on the water table, has been transported, or “smeared,” through soils due to a seasonally fluctuating water table. The smear zone is defined as a zone in soil, regardless of whether that soil is above or below the water table at any given time.

## Solubility

Solubility is the measure of the ability of a chemical to dissolve in water. See effective solubility.  
From the [Fate and Transport](#) chapter.

## Speciated

Analytical activity of identifying and/or measuring the specific forms of an element (such as a metal) defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure. For example, determining the amount of methyl lead vs. inorganic lead in a soil sample.  
From <http://www.speciation.net/Public/Document/2003/09/11/495.html>.

## Stakeholders

All parties with a direct or indirect interest in the outcome of an activity are stakeholders in that activity.

## Stratigraphy

Usually a description of the rock or soil strata in the subsurface, particularly the sequences of layers.  
From <http://www.topex.ucsd.edu/erth01/Glossary.html>

## Total dissolved solids (TDS)

Total dissolved solids (TDS) refers to the amount of inorganic materials such as minerals, salts, metals, cations, or anions dissolved in water. TDS is usually a measurement of the inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates) present in water.  
From <http://www.water-research.net/totaldissolvedsolids.htm>

## Unauthorized release

A release of petroleum into the environment (i.e., it escapes from the secondary containment, or from the primary containment, if no secondary containment exists).  
From California H&SC §25295.

## Unsaturated zone

The zone between the ground surface and the aquifer’s **water table** within which the moisture content is less than saturation and the pressure is less than atmospheric. In addition to water, the soil pore spaces in the unsaturated zone contain air or other gases. For an illustration, see the [Fate and Transport](#) chapter.  
From: [http://www.epa.gov/OUST/pubs/tum\\_appx.pdf](http://www.epa.gov/OUST/pubs/tum_appx.pdf)

**Vapor Pressure**

Vapor pressure or equilibrium vapor pressure is the pressure of a vapor in thermodynamic equilibrium with its liquid or solid forms in a closed container. The equilibrium vapor pressure is an indication of a liquid's evaporation rate. A substance with a high vapor pressure at normal temperatures is often referred to as volatile. See Henry's Law Coefficient.

**Vadose zone**

The vadose zone is the **unsaturated zone**.

**Volatile organic compound(s) (VOCs)**

Volatile organic compounds (VOCs) are organic chemical compounds with sufficiently high vapor pressures or Henry's Law Coefficient under normal conditions to significantly volatilize and enter the gaseous phase. The BTEX chemicals are VOCs.

**Water Quality Objectives (WQOs)**

Narrative or numerical criteria designed to define appropriate levels of environmental quality and to control activities that can adversely affect aquatic systems.

# Acronyms

Version 1.0 – Draft August 2010



## Scope of This Chapter

This is a complete list of acronyms in the California LUFT Manual, with their full spellings.

Every field has its own abbreviations and acronyms, and LUFT investigations and their participating disciplines are no exception. Each term below has been fully spelled out when it first appears in a chapter, and is afterwards used only in its shortened form. The table below also references where the acronym was first referenced.

Acronym	Definition	First Referenced Chapter
µg/L	Micrograms per liter	Reports
µg/m <sup>3</sup>	Micrograms per cubic meter	Fate and Transport
AB	Assembly bill	Roles and Responsibilities
AFCEE	Air Force Center for Engineering and the Environment	Remediation
AHA	Activity Hazard Analysis	Health and Safety
APCD	Air pollution control district	Health and Safety
APH	Air-Phase Petroleum Hydrocarbons	Laboratory Analytical Methods
API	American Petroleum Institute	Risk Evaluation and Risk Management
APN	Assessor's parcel number	Reports
T S K Q	Aquifer properties: Transmissivity Storativity Hydraulic conductivity Flow rate	
ARCH	Air rotary casing hammer	Site Assessment
ART	Active Remediation Target	
AS	Air sparging	Remediation
AST	Aboveground storage tank	GeoTracker
ASTM	American Society for Testing and Materials	Site Assessment
atm-m <sup>3</sup> / mol	Atmosphere-cubic meter(s) per mole(s) [Henry's Law Constant]	Fate and Transport
ATSDR	Agency for Toxic Substances and Disease Registry	Introduction
bgs	Below ground surface	Tank Removal and Closure in Place
BMP	Best Management Practices	Health and Safety
BOE	Board of Equalization	UST Cleanup Fund
BPC	Business and Professions Code	Roles and Responsibilities
BTEX	Benzene, toluene, ethylbenzene, and xylenes	Fate and Transport
Cal/EPA	California Environmental Protection Agency	GeoTracker
CAP	Corrective Action Plan	Roles and Responsibilities
CARB	California Air Resources Board	Glossary
CCR	California Code of Regulations	Overview
CDC	Centers for Disease Control	Health and Safety
CEG	Certified Engineering Geologist	Work Plans
cfm	Cubic feet per minute	Fate and Transport
CFR	Code of Federal Regulations	Roles and Responsibilities
CFU	Colony Forming Unit	Remediation
CGI	Combustible gas indicator	Health and Safety
CHHSL	California Human Health Screening Level	Risk Evaluation and Risk Management
cm <sup>2</sup>	Square centimeter	Remediation
CMT	Continuous multi-channel tubing system	Site Assessment

Acronym	Definition	First Referenced Chapter
CO	Carbon monoxide	Glossary
COCs	Constituents of concern	Work Plans
COELT	U.S. Army Corps of Engineers Loading Tool	GeoTracker
cp, cP	centipoise (also centiPoise) (unit of measurement for viscosity)	Fate and Transport
CPS	Cleanup Program Sites	GeoTracker
CPT	Cone Penetration Testing	Site Assessment
CSM	Conceptual Site Model	Work Plans
CTE	Central tendency exposure	Risk Evaluation and Risk Management
DAF	Dilution-Attenuation Factor	Conceptual Site Model
1,2-DCA	1,2-Dichloroethane	Fate and Transport
DFA	Division of Financial Assistance (SWRCB)	UST Cleanup Fund
DHS	California Department of Health Services	Overview
DIPE	di-Isopropyl ether	Fate and Transport
DL	Detection limit	Reports
DMG	California Division of Mining and Geology	Site Assessment
DNR	Department of Natural Resources	Fate and Transport
DO	Dissolved oxygen	Fate and Transport
DoD	Department of Defense	GeoTracker
DPE	Dual-phase extraction	Fate and Transport
DPT	Direct-push technologies	Site Assessment
DQO	Data quality objective	Site Assessment
DRO	Diesel-range organics (C10 to C16 and C17 to C25)	Fate and Transport
DTSC	State of California Dept. of Toxic Substances Control	Laboratory Analytical Methods
DWR	California Department of Water Resources	Risk Evaluation and Risk Management
EC	Electrical conductivity	Remediation
ECD	Electron capture detector	Laboratory Analytical Methods
EDB	Ethylene dibromide (aka 1,2-Dibromoethane)	Fate and Transport
EDC	Ethylene dichloride (aka 1,2-DCA = 1,2-Dichloroethane)	Fate and Transport
EDD	Electronic data deliverable	GeoTracker
EDF	Electronic Deliverable Format™	GeoTracker
ELAP	Environmental Laboratory Accreditation Program	Work Plans
EM	Electromagnetic Induction	Site Assessment
EPA, USEPA	(U.S.) Environmental Protection Agency	Laboratory Analytical Methods
EPH	Extractable petroleum hydrocarbon	Laboratory Analytical Methods
ESI	Electronic submittal of information	GeoTracker
ESL	Environmental Screening Levels	Risk Evaluation and Risk Management
ETBE	Ethyl tert butyl ether	Fate and Transport
EtOH	Ethanol	Fate and Transport
FID	Flame ionization detector	Laboratory Analytical Methods
FY	Fiscal Year	UST Cleanup Fund
g/cm <sup>3</sup> or g/cc	Grams per cubic centimeter	Site Assessment
GC-ECD	Gas chromatography/ Electron capture detector	Laboratory Analytical Methods
GC-FID	Gas chromatography/ Flame ionization detector	Laboratory Analytical Methods
GC-MS	Gas chromatography/ Mass spectrometry	Laboratory Analytical Methods
GIF	Graphics interchange format	GeoTracker
GIS	Geographic information system	GeoTracker
GPR	Ground Penetrating Radar	Site Assessment
GRO	Gasoline-range organics (C4 to C10)	Laboratory Analytical Methods
GW	Groundwater	Remediation

Acronym	Definition	First Referenced Chapter
H&SC	Health & Safety Code	Overview
HASP	Health and Safety Plan	Health and Safety
HAZWOPER	Hazardous Waste Operations and Emergency Response	Health and Safety
HI	Hazard index	Risk Evaluation and Risk Management
HML	Hazardous Materials Laboratory	Laboratory Analytical Methods
HPC	Heterotrophic plate count	Remediation
HSA	Hollow-stem auger	Site Assessment
ICP-MS	inductively coupled plasma mass spectrometry	Laboratory Analytical Methods
ICs	Institutional controls	Remediation
ID	Inner diameter	Remediation
IDW	Investigation-derived waste	Health and Safety
ISCO	In-situ chemical oxidation	Remediation
ISEF	International Society of Environmental Forensics	Site Assessment
ITRC	Interstate Technology & Regulatory Council	Conceptual Site Model
JPEG	Joint Photographic Experts Group (file suffix)	GeoTracker
JSA	Job Safety Analysis	Health and Safety
LAB EDF	Laboratory Electronic Deliverable Format™	Laboratory Analytical Methods
LARWQCB	Regional Water Quality Control Board – Los Angeles Region	Site Assessment
LEL/LFL	Lower explosive (flammable) limit	Health and Safety
LIA	Local Implementing Agency	Roles and Responsibilities
LIF	Laser-Induced Fluorescence	Site Assessment
LIMS	Laboratory Information Management System	GeoTracker
LNAPL	Light non-aqueous-phase liquid	Laboratory Analytical Methods
LOC	Letter of Commitment	UST Cleanup Fund
LOP(s)	Local Oversight Program(s)	Roles and Responsibilities
LUFT	Leaking Underground Fuel Tank	Overview
LUSTIS	Leaking Underground Storage Tank Information System	GeoTracker
MADEP	Massachusetts Department of Environmental Protection	Site Assessment
MCL	Maximum Contaminant Level	Conceptual Site Model
mg/kg	Milligrams per kilogram	Reports
mg/L	Milligrams per liter	Fate and Transport
MIP	Membrane Interface Probe	Site Assessment
mL	Milliliter	Laboratory Analytical Methods
mL/min	Milliliters per minute	Site Assessment
mm	Millimeter	Site Assessment
mm Hg	Millimeters of mercury	F&T
MS	Mass spectrometry	Laboratory Analytical Methods
MSDS	Material Safety Data Sheet	Health and Safety
MTBE	Methyl tertiary butyl ether	Fate and Transport
NAPL	Non-aqueous-phase liquids	Health and Safety
ND	Non-detectable	Reports
NFA	No Further Action	Introduction
NFAR	No Further Action Required	Reports
NPDES	National Pollutant Discharge Elimination System	Health and Safety
NSOs	Heterocyclic compounds (nitrogen, sulfur, oxygen)	Fate and Transport
NYSDOH	New York State Department of Health	Site Assessment
O&M	Operation and maintenance	Corrective Action Plan
OEHHA	Office of Environmental Health Hazard Assessment	Risk Evaluation and Risk Management
ORO	Oil-range organics (C25 to C32)	Fate and Transport
ORP	Oxidation/reduction potential	Site Assessment
OSHA	Occupational Safety and Health Administration	Health and Safety

Acronym	Definition	First Referenced Chapter
OSWER	Office of Solid Waste and Emergency Response	Site Assessment
OUST	Office of Underground Storage Tanks	Remediation
PAHs	Polycyclic aromatic hydrocarbons	Fate and Transport
PCE	Perchloroethene (also perchloroethylene)	Fate and Transport
PDF	Portable document format	GeoTracker
PG	Professional Geologist	Work Plans
PIANO	Paraffins, Isoparaffins, Aromatics, Naphthenes (cycloalkanes), and Olefins	Site Assessment
PID	Two uses of PID as an acronym in this Manual: Particle Impact Drill Photo-Ionization Detector	Site Assessment Tank Removal and Closure in Place
PLC	Programmable logic controller	Remediation
POTW	Publicly owned treatment works	Corrective Action Plan
ppb	Parts per billion	Vapor Intrusion
PPE	Personal protective equipment	Health and Safety
ppm	Parts per million	Remediation
ppm(v)	Parts per million by volume	Remediation
ppt	Parts per trillion	Vapor Intrusion
PRGs	Preliminary Remediation Goals	Risk Evaluation and Risk Management
psig	Pounds per square inch gauge	Remediation
PVC	Polyvinyl chloride	Site Assessment
QA	Quality assurance	GeoTracker
QC	Quality control	Work Plans
RBCA	Risk-based corrective action	Fate and Transport
RCE	Registered Civil Engineer	Work Plans
RCRA	Resource Conservation and Recovery Act	Risk Evaluation and Risk Management
RfD	Reference dose	Fate and Transport
RME	Reasonable maximum exposure	Risk Evaluation and Risk Management
ROI	Radius of influence	Remediation
ROST	Rapid Optical Screening Tool	Site Assessment
RP	Responsible Party	Overview
RSLs	Regional Screening Levels	Fate and Transport
RWQCB	Regional Water Quality Control Board	Roles and Responsibilities
SB	Senate Bill	UST Cleanup Fund
SC	Site Cleanup	GeoTracker
scfm	Standard cubic feet per minute	Remediation
SCVWD	Santa Clara Valley Water District	Fate and Transport
SED	Science and Ecosystem Support Division	Site Assessment
SFRWQCB	San Francisco Bay Regional Water Quality Control Board	Laboratory Analytical Methods
SGC	Silica-gel cleanup	Fate and Transport
SIM	Single Ion Monitoring	Laboratory Analytical Methods
SLIC	Spills, Leaks, Investigations, and Cleanups	GeoTracker
SOP	Standard operating procedure	Work Plans
SOW	Scope of work	Work Plans
SPH	Separate-phase hydrocarbons	Site Assessment
SSD	Sub-slab depressurization system	Vapor Intrusion
SVE	Soil-vapor extraction	Risk Management and Risk Evaluation
SVOC	Semi-volatile organic compound	Remediation
SWPPP	Stormwater Pollution Prevention Plan	Work Plans
SWRCB	State Water Resources Control Board <i>[preferred]</i> , State Water Board	Overview

Acronym	Definition	First Referenced Chapter
TAME	Tertiary amyl methyl ether	Fate and Transport
TBA	<i>t</i> -Butyl alcohol	Fate and Transport
TCLP	Toxicity Characteristic Leaching Procedure	Laboratory Analytical Methods
TEL	Tetra ethyl lead (also “tetra ethyllead”)	Fate and Transport
TIC	Tentatively identified compound	Laboratory Analytical Methods
TIFF	Tagged image file format	GeoTracker
TML	Tetra methyl lead (also “tetra methyllead”)	Fate and Transport
TPH	Total petroleum hydrocarbon	Fate and Transport
TPHCWG	Total Petroleum Hydrocarbons Criteria Working Group	Laboratory Analytical Methods
TPHd/mo	Total petroleum hydrocarbons as diesel or motor oil	Fate and Transport
TRPH	Total recoverable petroleum hydrocarbons	Laboratory Analytical Methods
TSD	Treatment, storage, and disposal	Tank Removal and Closure In Place
UCL	Upper confidence limit	Risk Evaluation and Risk Management
UEL/UFL	Upper explosive (flammable) limit	Glossary
USCG	U.S. Coast Guard	Health and Safety
USCS	United Soil Classification System	Work Plans
USGS	U.S. Geological Survey	Reports
UST	Underground storage tank	Overview
USTCF	UST Cleanup Fund	UST Cleanup Fund
VI	Vapor intrusion	Site Assessment
VOA	Volatile Organic Analysis	Laboratory Analytical Methods
VOC	Volatile organic compound	Fate and Transport
VPH	Volatile petroleum hydrocarbon	Laboratory Analytical Methods
VVLs	Valid Value Lists	GeoTracker
WQOs	Water Quality Objectives	Reports
WSF	Water soluble fraction	Fate and Transport



## **CALIFORNIA LUFT MANUAL**

### **APPENDIX A**

#### **LUFT SCREENING LEVEL DEVELOPMENT**

##### **DETAIL AND CALCULATIONS**

**Note to Reader: The detail and calculations are undergoing per review and will be available after the release of the Manual for public comment**

# **CALIFORNIA LUFT MANUAL**

## **APPENDIX B SOIL BORING DESCRIPTION**

## Appendix B

### Soil Boring Description

This appendix provides additional guidance to that discussed in the Manual regarding proper logging of a soil boring.

#### Minimum Background for Well-Site Geologists

The well-site geologist should have a practical understanding of mass wasting, soil forming, and depositional processes sufficient to predict likely sub-surface geology based on site setting. The geologist should be able to interpret geomorphology from local topography, comprehend relevant technical literature, and correlate drilling and hydrographic results from nearby sites. If the geologist lacks specific academic training, numerous practical references are available; examples include Fetter 2000, Rahn 1996, Miller and Donahue 1990, Reading (ed.) 1978, Blatt, Middleton, and Murray (1980), LeRoy and LeRoy (ed.) 1987, and Tearpock and Bischke (1991). The geologist should also have current HAZWOPER training and familiarity with drilling methods.

Project managers should require well-site geologists to write drilling prognoses prior to each phase of investigation. Prognoses should, at a minimum, include total depth of investigation, depths to free seepage and refusal as appropriate, depths, thicknesses, and hydraulic conditions of permeable units, target sampling intervals, and potential mechanical and chemical health and safety issues.

#### Core Handling and Preservation

The driller should provide an appropriate working area, with direct line of sight to the drilling crew, and appropriate support personnel and tools to assemble, disassemble, and decontaminate samplers and assist with core handling.

The well-site geologist should at minimum have the following equipment:





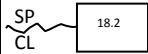
- Personal protective equipment
- Site safety plan
- Core record, logging, and monitoring well as-built forms
- Pollutant field-screening equipment, e.g., calibrated PID
- Appropriate soil and groundwater sampling equipment, i.e., soil sampling supplies, coolers, coolant, packing material, and disposable bailers
- Water level indicator
- Soil knives
- Weighted fiberglass measuring tapes
- Appropriate core storage, i.e., boxes and dividers
- Coring run labels
- Hand lens
- Munsell soil color charts
- Grain texture and composition estimation charts
- Dropper bottle with dilute hydrochloric acid (HCl)
- Graduated flask
- Squirt bottle
- Digital camera
- Appropriate core flags, e.g., colored toothpicks
- Wide, clear adhesive tape
- Permanent markers
- Ice cube trays or watercolor pallet

During drilling, the well-site geologist should focus on maintaining depth-accurate core recovery, preserving core, and recording gross lithology changes and related drilling breaks. Other duties often include field screening for pollutants,

sampling soils for potential laboratory analyses, monitoring for seepage, observing drill rig behavior, assisting with sampler decontamination, tracking investigation-derived wastes, and controlling drilling area access. During typical shallow borings with short trip-out times after each sample, insufficient time exists during drilling to focus on detailed logging.

Prior to drilling, the geologist should set up core boxes and dividers, marking dividers with arrows pointing up-core. To avoid storing cores upside-down, the geologist *must* communicate desired core orientation clearly to support crew. During drilling, the well-site geologist should gather preliminary information while the core is in the barrel, direct sample collection and transfer of cores into storage, label coring runs, and record information on a Core Record Sheet; see Table 4, a partial form. Actual forms would call for further information—typically in the header or footer; for example, project name, date, time, location, drilling method and contractor, and geologist.

Table B1: Example Core Record Sheet

Coring Run	Depth Penetrated (feet)	Feet Cut	Feet Recovered	Feet Not Recovered	PID Reading (ppmv)	Sample Number	Moisture	Lithology	Remarks
1	0 to 3.4	3.4	1.2	2.2	60, bottom of run	nnnn <sup>1</sup> , 0.9 to 1.2, 10:30	dry	Asphalt  Fill	Bottle cap in fill
2	3.4 to 8.4	5.0	3.4	1.6	70, bottom of run	nnnn, 6.3 to 6.8, 10:35	Slightly moist	CL  ML	Driller added sand catcher after Run#2
3	8.4 to 13.6	5.0	4.5	0.7; see remarks.	15, bottom of run	nnnn, 8.6 to 8.9 11:00	Slightly moist	ML  SM	Muscovite <sup>1</sup> Driller extended shoe 0.2' beyond run
4	13.6 to 18.6	5.0	5.0	0	200, at contact, SP/CL	nnnn, 18.2 to 18.5, 11:15	Moist  Very Moist	SM  	Bedforms <sup>2</sup>  Bedforms <sup>2</sup> Slight fuel odor

## Notes:

CL: Clay

ML: Silt

nnnn: Example sample #

ppmv: part per million vapor

SM: Silty sand

SP: Poorly graded sand

1. Abundant muscovite in silt, 8.6 to 8.9

2. Bedforms, Run #4, in SM, 13.6 to 14.2, even parallel, continuous, laminae, 1 to 5 mm, sharp, with heavy mineral segregation. Also in SP, 16.5 to 17.2, uneven, nonparallel, discontinuous, faint, in sets about 2 to 5 cm, photographs taken, co-sets marked in frames.

In the example above, it is important to note that *Coring Run*, *Depth Penetrated*, *Feet Cut*, and *Feet Not Recovered* are depths penetrated relative to grade surface. The depths are measured, precise to the nearest 1/10 foot (~ one inch). For maps and cross sections, in normal drilling environments, for example HSA in alluvium, one can usually later assume depth-accuracy to within about ½ foot.

The geologist should mark a corresponding core label with information in the first four columns, and place it in core storage at the bottom of each run. While no-recovery intervals are usually at the tops of core barrels, most geologists typically assume footage not recovered is from the bottoms of coring runs. This is generally correct, but exceptions can occur, for example, due to a partially obstructed sampler shoe, slough, and heaving sands. To avoid inaccuracies, the geologist should communicate closely with the driller.

Note also the columns titled *PID Reading*, *Sample Number*, and *Moisture*. On Coring Run #4, the PID reading and sample are from a specific geologic contact, and reflect a judgmental sample. Notes in the *Moisture* column reflect conditions during drilling.

Columns titled *Lithology* and *Remarks* are key to accurate core description. The well-site geologist should fill these in prior to removing the core from the barrel. Dashed lines in the *Lithology* column depict gradational contacts, solid lines, sharp contacts. The contact at 18.2 feet below grade surface, a wavy solid line, is a scour surface. To avoid inaccurate measurements, the well-site geologist should scrape core with a soil knife to get through zones affected by frictional smearing. Notes in the *Remarks* column in this case show evidence of fill, drilling actions, and, importantly, sedimentary structures likely to be disturbed during removal of core from the barrel. For example, on Core Run #4, see especially the remark “bedforms,” and related Footnote 2.

Sedimentary structures and textures are difficult to preserve while transferring core into ambient storage. To keep pace with the driller, the well-site geologist must develop techniques to quickly describe core in the barrel. For example, one can apply a strip of clear adhesive tape to sands, annotating features with a waterproof marker, and retaining the strip for later detailed logging. To describe graded beds, one can collect sub-samples at discrete depths, for example into an ice-cube tray or watercolor palette. For bedforms (e.g., laminae, ripples, cross-bedding, etc.), the McKee and Weir (1953) classification system is recommended, as used in Footnote 2. One can also digitally photograph core, marking key features with appropriate core flags.

### Follow-Up Detailed Logging

All logged intervals should at minimum begin with ASTM/USCS Group Symbols and Group Names, followed by Munsell Colors, text plus hue, value, and chroma codes. For fine-grained soils,  $\geq 50\%$  finer than #200 sieve, descriptions should at minimum continue with plasticity, toughness, and dilatancy. As appropriate, descriptions should also include reaction with HCl, *soil* (pedogenic) structures, cementation, root bores, and accessory minerals. For silts, Group Symbol ML, especially those with Group Names *Silt with Sand*, and *Sandy Silt*, also log appropriate *sedimentary* structures.

For coarse-grained soils (sediments),  $< 50\%$  finer than #200 sieve, descriptions should continue with texture, composition, and sedimentary structures. Texture should generally include total size range and modes, in millimeters (mm), grain shape, using the Powers (1953) chart for sands, USCS/ASTM for gravels, and estimated sorting. Efficient estimates of grain size distributions are feasible in the field; we suggest conducting water-settling tests in a graduated cylinder. Textural descriptions should be sufficient to describe vertical grading within permeable units (e.g., fining- and coarsening-upward sequences).

Composition should include hand-lens estimated percentages of quartz, feldspars, and rock fragments, normalized for sand and larger particles. Composition should also include accessory minerals (e.g., heavy minerals and muscovite) and fossils. For gravels, descriptions should be reasonable based on hand lens description, but sufficient to correlate to local outcrops at basin margins. For example, “granitoid with modal sodic feldspar and dark minerals” would be reasonable; further details, such as specific mineralogy, would be questionable based solely on a hand lens description.

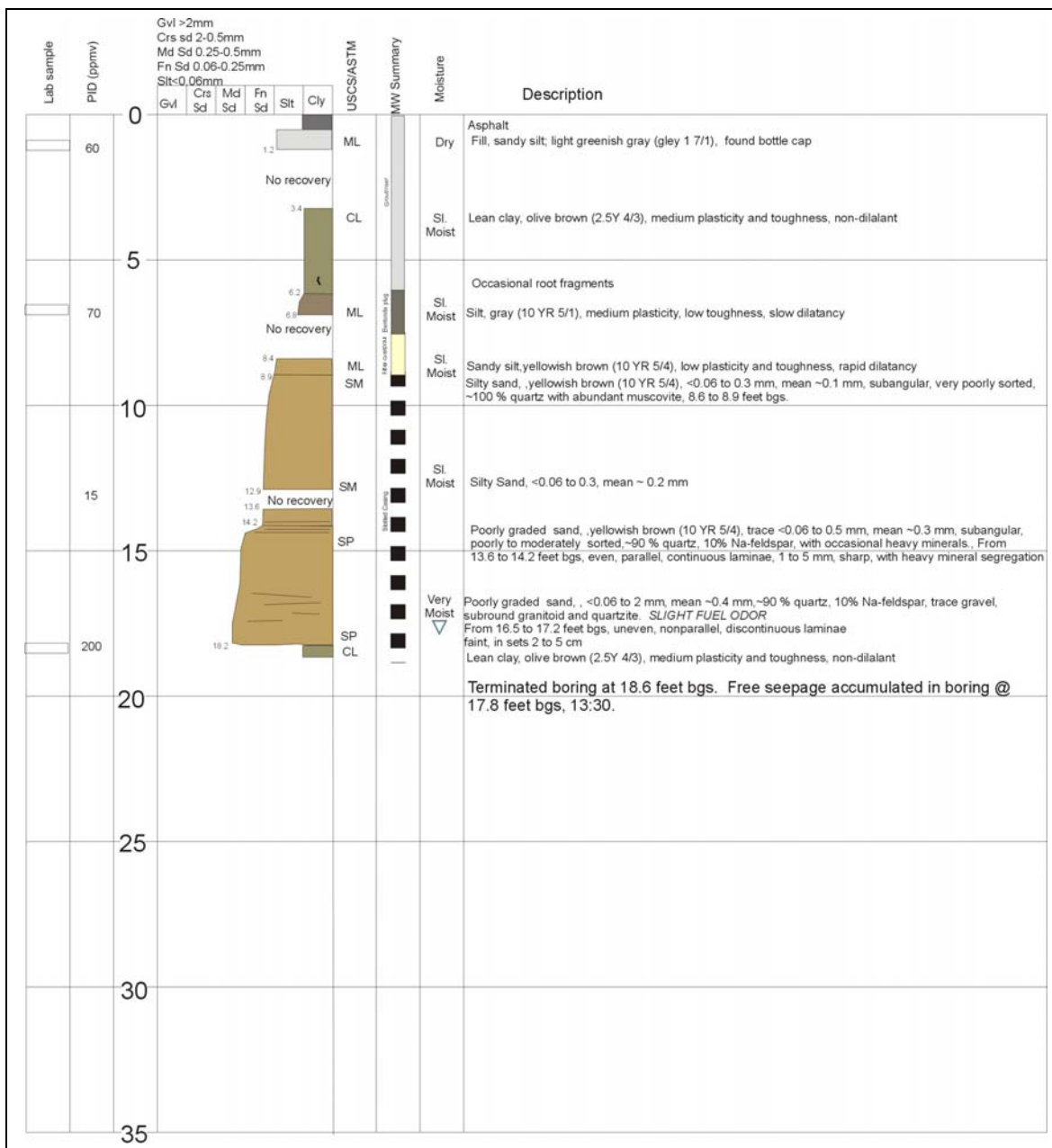
Sedimentary structures are bedding, bedforms, soft sediment deformation features, and trace fossils. Bedding descriptions should generally include thicknesses of sets and co-sets. Descriptions of bedforms should be sufficient to allow reasonable estimates of depositional flow velocities. Soft sediment deformation features, such as load casts and convoluted bedding, occasionally found in core, can provide evidence of rapid burial of an under-compacted substrate. Trace fossils, for example escape burrows and feeding traces, can likewise indicate burial history.

Descriptions of coarse-grained intervals, based on texture, composition, and sedimentary structures, should in general be sufficient to allow reasonable interpretation of depositional environment (e.g., alluvial fan, braided stream, point bar, estuary, beach, etc.).

All descriptions should end with, or otherwise emphasize, field moisture content and evidence of pollution. Evidence of pollution, staining, odor, and sheen, should appear in italics.

Various formats exist for boring logs. Most useful formats show on each page: the graphics of permeable units, monitoring-well construction summaries, and first free seepage observed while drilling. Figure B1 is an example log, based on the above core record sheet. This is a partial form; typical header information, which has been omitted, includes project name, location, date, time, drilling and sampling methods, contractor, geologist, surface elevation, etc. Also note that detailed monitoring well as-builts should accompany logs.

Figure B1: Example of a Boring Log



The above log indicates a point bar, a commonly encountered sand deposit, from about 6.8 to 18.2 feet below grade surface. Top of the deposit is an inference based on a lost core, assumed to have fallen from the barrel due to lack of cohesion. Based on depth to free seepage, the sand is likely hydraulically unconfined. Because the slotted casing interval extends nearly to the top of the sand, and the water table might rise, slotted casing and filter media choice should account for the finest-grained portion of the deposit.

Assuming the point bar is 11.4 feet thick (h), roughly similar to bank-full channel depth, and the channel is highly sinuous, the approximate width (w) of the sand body in the subsurface is;  $w = 6.8h^{1.54}$ , around 290 feet (Leeder 1973). Its shape is likely lunate, roughly a half-moon. Because gravels near the base of the deposit include granitoid rocks, one could assume the deposit came from an intrusive igneous source, which could narrow the search direction for the edge of the sand. At the convex margin of the sand, one might expect an oxbow plug, a fat clay that could greatly affect remedial system performance.



An experienced, adequately trained well-site geologist can typically generate a description similar to the above in about one hour. Description heavily relies on proper core handling and preservation.

# **CALIFORNIA LUFT MANUAL**

## **APPENDIX C VAPOR INTRUSION**

## Appendix C

### Vapor Intrusion

This appendix discusses the Vapor Intrusion (VI) pathway for petroleum hydrocarbons at leaking underground fuel tank (LUFT) sites.

#### Warning!

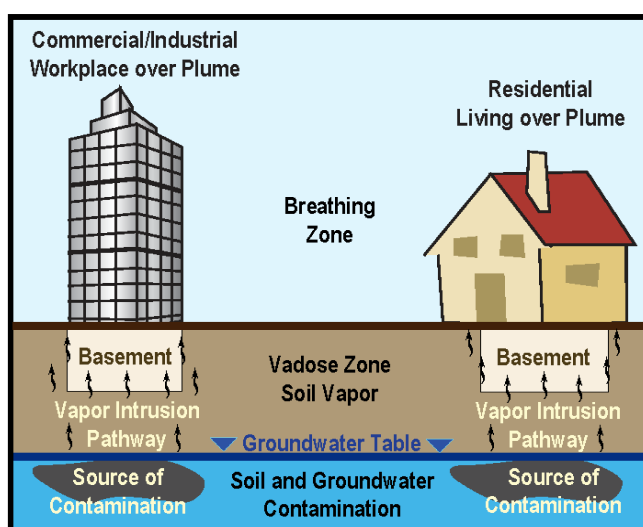
The assessment methodologies described herein may not be appropriate to address conditions of immediate concern such as explosion hazard or acute health impacts. If petroleum hydrocarbon odors are reported for a structure, or if field screening indicates volatile organic compound (VOC) concentrations where flammability concerns are raised (e.g., concentrations greater than 10% lower explosive limit [LEL]), then prompt action to protect the building and occupants should be taken.

Vapor intrusion (VI) is the term used to describe the migration of VOCs from sub-surface soil and/or groundwater upward, via soil vapor, into buildings, potentially causing an unacceptable chemical exposure for building occupants (State of California Department of Toxic Substances Control [DTSC]/California Environmental Protection Agency [Cal/EPA] 2005).

When a petroleum release occurs at a LUFT site, petroleum is typically released as a light non-aqueous-phase liquid (LNAPL). LNAPL moves vertically downward through the unsaturated zone in response to gravity and capillary forces until either a relatively impermeable zone or the water table is encountered. Several factors, including the volume of the release, rate of the release, hydraulic conductivity of the soils, depth to the water table, and adsorptive capacity of the subsurface materials, will determine whether LNAPL will ultimately migrate downward to the area of the capillary fringe and the water table or will remain entirely in the vadose zone. As partitioning from liquid to vapor phase takes place, vapors migrate vertically (upward) toward the ground's surface. The migration of the contaminants may pose a threat to occupants living or working above the source of contamination.

Figure C1 illustrates the VI pathway in a commercial and residential setting. As the figure illustrates, constituents of concern (COCs) travel in the vapor phase from the source of contamination through the vadose zone into the breathing zone.

Figure C9 – Vapor Intrusion Pathway



### Background

The potential adverse effects to human health by VI due to VOCs in soil, groundwater, and soil vapor garnered significant attention from regulatory agencies in the late 1990s. Over the past decade many agencies, including the United States

Environmental Protection Agency (USEPA), DTSC, the California Regional Water Quality Control Boards (RWQCB), State and local regulatory agencies have provided guidance on how to address the issue of VI.

The State Water Resources Control Board (SWRCB) has not issued any regulations that explicitly address the issue of VI or that set clean-up standards to ensure that indoor air quality is not adversely affected by petroleum vapors from soil or groundwater contamination. The DTSC and the North Coast, Los Angeles, and San Francisco RWQCBs have each developed guidance documents that address VI in varying degrees. Most of these guidance documents are generally based in part on the California DTSC guidance. The North Coast RWQCB and DTSC provide comprehensive guidance documents for assessing the potential of VI. It is important to note that these guidance documents address all types of contamination, not just contamination from petroleum USTs.

## History.

The following are significant guidance documents or events that represent milestones in VI development and understanding.

- 1991 – Johnson-Ettinger Model published
- 2000 – USEPA holds Washington D.C. Vapor Summit
- 2002 – USEPA Subsurface VI Guidance
- 2004/2005 – DTSC VI Guidance Document
- 2007 – Interstate Technology & Regulatory Council (ITRC) VI Practical Guideline
- 2007 – ITRC VI Scenario Document
- 2007/2008 – American Society for Testing and Materials (ASTM) VI Standard Practice

## Further Reading.

The following references are useful to evaluate the potential for VI and provide details on the VI pathway, methodology for investigation, and options for mitigation

- USEPA, 2002. Office of Solid Waste and Emergency Response ([OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils \(Subsurface Vapor Intrusion Guidance\)](#)) November 2002.
- DTSC, 2005. [Interim Final Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air](#). February 7, 2005.
- [ITRC, 2007. Vapor Intrusion Pathway: A Practical Guideline. January 2007.](#)
- [ASTM, 2008. ASTM E2600 - 08 Standard Practice for Assessment of Vapor Intrusion into Structures on Property Involved in Real Estate Transactions.](#)

## Conceptual Site Model

The VI pathway evaluation should be conducted in a manner consistent with the Conceptual Site Model (CSM). The CSM describes the contaminant sources, transport/ migration pathways, and receptors/exposure pathways for the site. In order for the VI pathway to be complete, each of these CSM components must be present. If a petroleum source is not present in soil or groundwater, or a continuous migration pathway from the source to the surface is not present, or if there are no structures for the receptors, then the pathway can be eliminated from further consideration.

The conceptual model for the VI pathway for petroleum hydrocarbons includes the following potential fate-and-transport mechanisms.

- Volatilization of constituents from soil or groundwater to soil gas;
- Diffusion of the constituents in soil gas through the vadose zone;
- Biodegradation of the constituents within portions of the vadose zone with sufficient oxygen to promote aerobic biodegradation
- Convection of soil gas into the structure through cracks and/or openings in the building foundations; and
- Mixing of the constituents within the structure due to building ventilation.

Source characteristics considered in the conceptual model for VI for LUFT sites include the following information:

- Identification of COCs;
- Concentrations of the constituents in the impacted media;
- Lateral and vertical distances between the bottom of the building and the impacted soil, groundwater or product (e.g., is the soil beneath the building impacted or not?).

Pathway characteristics considered in the VI conceptual model include the following information and are further discussed in the Vapor Migration Pathway Section below:

- Soil properties affecting diffusion of constituents through the vadose zone (e.g., soil type, total porosity, and water-filled porosity);
- Evidence of zones favorable for aerobic biodegradation (i.e., presence of oxygen in the subsurface);
- Building characteristics (commercial/residential building, distance from impacted soil/ groundwater to the building, type of building foundation, details about the presence of cracks, whether the building has a basement or not);
- Surface cover at site (asphalt, concrete, soil, grass);
- Building ventilation properties that may affect convection of soil gas into the structure (e.g., positively pressurized building, ventilation air exchange rate) and mixing in the building;
- Corrective measures in place that may limit migration of constituents into building (e.g., source remediation, mitigation measures such as a vapor barrier).

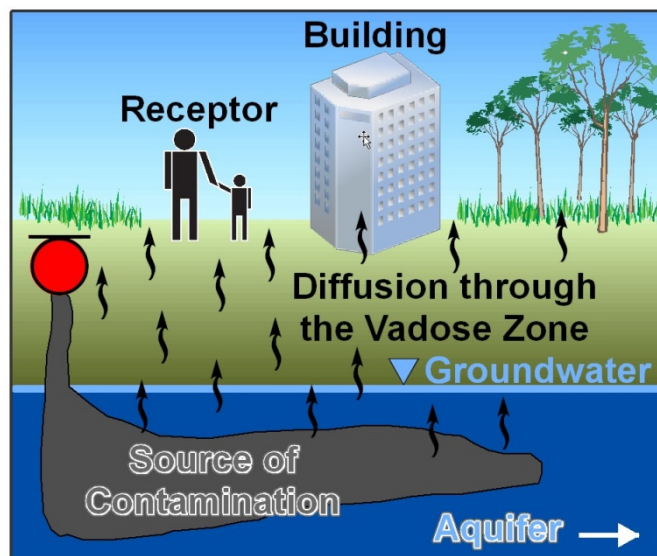
Receptor characteristics considered in the VI conceptual model include the following information:

- Building occupant type (e.g., commercial, residential);
- Age of occupants (e.g., children, adults);
- Existing or potential future buildings.

Exposure assumptions or characteristics considered in the VI conceptual model include the following information:

- Daily time frame (e.g., 8 hours per day, 24 hours per day)
- Duration (e.g., 30 years, 70 years)

**Figure C10 –Source, Pathway, Receptor**



## Evaluation of Complete Vapor Migration Pathway

In order to assess the potential risks of VI into surrounding buildings, it is important to identify whether the vapor migration pathway is complete. VI pathway assessments for petroleum hydrocarbon sites differ from evaluations for chlorinated VOC sites, because petroleum hydrocarbons can readily degrade under aerobic conditions in the vadose zone. It is universally accepted that soil microbes which degrade petroleum-based hydrocarbons are ubiquitous in soil. Under the appropriate conditions, the rate of biodegradation in the vadose zone may be sufficient to cause the vapor migration pathway to be incomplete (Davis 2009). Those conditions include:

- Adequate oxygen in the soil (4%);
- Clean soil between the contamination and affected building (greater than 5 feet);
- Low dissolved levels of contamination (<1,000 micrograms/liter [ $\mu\text{g/L}$ ] benzene, <10,000  $\mu\text{g/L}$  total petroleum hydrocarbons [TPH]).

The degradation of petroleum hydrocarbons has been well documented in the literature. Studies (American Petroleum Institute [API] 2009; Davis 2006) have shown that the VI pathway is insignificant for dissolved-plume petroleum hydrocarbon sources or deep petroleum hydrocarbon sources (including LNAPL sites), provided there is a zone of aerobic, non-impacted soils beneath the building sufficient for bioattenuation of the diffusing hydrocarbons.

It is important to note that there are other site characteristics which could cause the pathway to be incomplete, such as VOCs not volatilizing from groundwater or lithology inhibiting soil vapor migration upwards. A site assessment including soil-gas sampling for the presence of oxygen and carbon dioxide (a by-product of the biodegradation process) should be completed to properly ascertain whether sufficient biodegradation of petroleum vapors is occurring in the vadose zone.

### Preferential Pathways

When evaluating whether the vapor migration pathway is complete, it is important to consider preferential pathways, physical site conditions that can be an avenue for soil-vapor migration. These avenues may complete the vapor migration pathway, even when the pathway screening criteria appear to be satisfied. Examples of preferential pathways:

- Large underground utility trenches (storm drains)
- Fractured bedrock
- Basement sumps
- Elevator shafts
- Large utility vaults

If a source of VOCs, migration/transport pathways, and receptor and exposure pathways all exist, then risks may need to be assessed at a LUFT site. In some cases, a relatively simple screening process may be used to evaluate the VI pathway; for example, the Johnson & Ettinger Lite model on-line calculator screens for potential VI from groundwater

([http://www.epa.gov/athensr/learn2model/part-two/onsite/InE\\_lite.html](http://www.epa.gov/athensr/learn2model/part-two/onsite/InE_lite.html)).

In other cases, a more detailed assessment may be necessary as discussed in the VI Pathway Screening section below.

### Biodegradation of Petroleum Hydrocarbons

As discussed in the Fate and Transport chapter of this Manual, petroleum hydrocarbons naturally biodegrade under both aerobic and anaerobic conditions. The simplest, most water-soluble constituents are biodegraded first (e.g., benzene, toluene, ethylene, xylene [BTEX], and the small n-alkanes); the more complex molecular structures are biodegraded more slowly. Bacteria ubiquitous in the environment cause the biodegradation.

These bacteria are important in the natural attenuation of dissolved hydrocarbons, serving to limit the migration of VOCs in groundwater to a distance of less than 100 meters (m) (320 feet) at 90% of release sites studied (Newell and Connor 1998).

The bacteria are equally effective in the vadose zone. A number of field studies have documented the biodegradation of petroleum constituents in the vadose zone (e.g., Davis et al. 2009, API 2001, Pasteris et al. 2002, Lundegard and Johnson 2006, Davis 2006). DeVaul, in his 2007 publication, *Indoor Vapor Intrusion with Oxygen-Limited Biodegradation for a Subsurface Gasoline Source*, compiled aerobic hydrocarbon biodegradation rates in vadose-zone pore-water from numerous studies. Although the reported degradation rates varied between studies, within the gasoline range (i.e., C6 to C12 hydrocarbons), the only clear difference by hydrocarbon class was between aromatic and aliphatic hydrocarbons. DeVaul reported a geometric mean degradation rate of 0.79/hour for aromatic hydrocarbons (based on 84 data sets) and 71/hour for aliphatic hydrocarbons (straight chain and branched, based on 17 data sets). These groups do not include fuel additives such as methyl tert-butyl ether (MTBE).

Several model studies of petroleum VI that account for aerobic biodegradation have evaluated the combined impact of oxygen demand and degradation rate on petroleum VI (Parker 2003; Abreu and Johnson 2006; DeVaul 2007; Abreu et al. 2009). For the evaluations conducted by Abreu et al. (2009), petroleum vapor attenuation was not oxygen-limited for vapor source concentrations less than 10,000,000 micrograms per cubic meter ( $\mu\text{g/m}^3$ ) or 10 milligrams per liter (mg/L). In the

cases where attenuation was not oxygen limited, the distance required between the building foundation and the dissolved petroleum source to ensure high petroleum VOC attenuation depended on the first-order degradation rate. When using the geometric mean biodegradation rate for aromatic hydrocarbons (0.79/hour), a separation distance between the source and the building of 1 m (3 feet [ft]) was sufficient to achieve 100x bioattenuation (i.e., a 100x increase in attenuation relative to the “no biodegradation” case), while a separation distance of 3 m (10 ft) resulted in 10,000x bioattenuation. When using the lower degradation rate (0.79/hour), a separation distance of 3 m (10 ft) was required to achieve 100x bioattenuation.

The modeling conducted by DeVaul (2007) indicates a similar range of bioattenuation. Based on the range of aerobic diffusion reaction lengths (i.e., the distance over which the concentration is reduced by 50%) reported for benzene (2.3 to 29 centimeters [cm]), the bioattenuation expected to occur over a distance of 3 m is at least 1000x (API 2009).

The available scientific literature related to petroleum vapor fate, transport, and intrusion into buildings suggests that:

- 1) a number of mechanisms facilitate the transport of oxygen below building foundations, resulting in aerobic conditions at many sites, and
- 2) aerobic vadose-zone petroleum hydrocarbon biodegradation occurs wherever sufficient oxygen is present, resulting in rapid attenuation of hydrocarbon vapors.

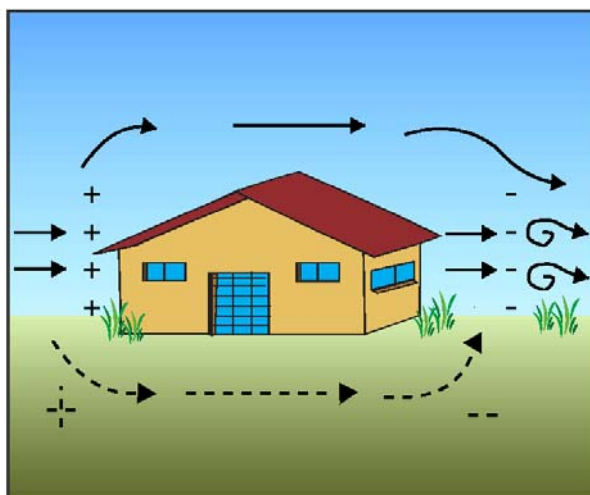
As a result, aerobic biodegradation often serves as a barrier to petroleum VI at the majority of sites with sufficient separation between the source and the building foundation.

### Oxygen Transport below Buildings

Often a building's foundation serves as a barrier to oxygen entry into the vadose zone; however, a number of mechanisms have been identified that can transport oxygen from the atmosphere into the subsurface below a building foundation. When wind strikes a building, a pressure gradient is created, with higher pressure on the upwind side and lower pressure on the downwind side of the building, as shown in Figure C3.

This pressure gradient can result in advection of atmospheric air through the soil below the building, transporting oxygen from the atmosphere into the shallow soil gas, thereby allowing for aerobic biodegradation (Lundegard et al. 2008, Fischer et al. 1996).

**Figure C11 – Pressure Gradient Created by Wind on a Building**



Luo and others present soil gas concentration profiles for TPH and oxygen over the footprint of a building overlying petroleum hydrocarbon-impacted soils. These data indicate a spatial correlation between the dominant wind direction and concurrent low concentrations of TPH and high concentrations of oxygen (Luo et al. 2009).

In addition to wind-driven oxygen transport, in buildings with continuous or transient positive pressure conditions, air will flow from the building to the shallow soils through any foundation cracks or other penetrations, providing an additional source of oxygen below the foundation (McHugh et al. 2006). Many commercial buildings are maintained at a positive



pressure relative to the atmosphere by the HVAC system, and passively ventilated buildings (e.g., typical single-family residences) typically fluctuate between positive and negative pressure due to wind effects and other transient conditions.

## Pathway Screening

As discussed above in the CSM Section of this chapter, if a LUFT site has a confirmed source of VOCs, complete migration/transport pathways, and receptor and exposure pathways, then the vapor pathway needs to be further screened.

There are a number of criteria to be considered when evaluating a site for VI. Table C1 may be used as a screening tool or a comparison with screening levels (provided by the regulatory agency with jurisdiction over the case) may be considered.

Scientific understanding of how vadose-zone biodegradation serves as a barrier to petroleum VI supports the pathway screening criteria presented in Table C1; however, care must be used in identifying preferential pathways or uncharacterized source areas that could cause VI impacts, even when the pathway screening criteria appear to be satisfied.

The objective of a VI pathway screening is to evaluate whether the site requires further action, such as additional sampling or mitigation.

## Vapor Intrusion Risk Screening Tool

The Risk Management chapter of this manual describes a “Vapor Intrusion Risk Screening Tool” which is a distillation of the information presented in Table C1. A LUFT site is assumed to present no unacceptable risk from vapor intrusion if the following site conditions are met:

- (1) *For soil sources and low-strength groundwater sources:* 5 feet or more of clean soil between the bottom of the building and the shallowest impacted soil or impacted groundwater.
- (2) *For high-strength groundwater sources:* 10 feet or more of clean soil between the bottom of the building and the shallowest impacted soil or impacted groundwater.
- (3) *For measurable free product on the water table:* 30 feet or more of clean soil between the bottom of the building and the water table.

A low-strength groundwater source is defined as *dissolved phase* benzene groundwater concentrations below 1000 micrograms per liter (ug/L) and *dissolved phase* TPH concentrations below 10,000 ug/L. A high-strength groundwater source is defined as dissolved concentrations of benzene greater than 1000 ug/l and *dissolved phase* TPH concentrations greater than 10,000 ug/l.

In the unsaturated zone, clean soil is defined as TPH concentrations less than 100 mg/kg, PID readings of less than 10 ppm, or oxygen present concentrations >4%. Under these conditions, it is assumed that natural attenuation is sufficient to mitigate concentrations of volatile petroleum constituents. Conversely, if these conditions do not apply at a particular LUFT site, a site-specific soil vapor intrusion and risk evaluation may be required.

Table C17 – Vapor Intrusion Pathway Screening at Petroleum Hydrocarbon Sites

Source Characteristics within 30 Feet of Building	Likelihood of Risk Associated with Vapor Intrusion	Recommended Evaluation	Basis for Recommendation	Potential Confounding Factors
LNAPL within 30 feet of building structure or dissolved petroleum hydrocarbons in direct contact with building structure	High	Evaluation of safety/explosion hazards. Building evaluation and mitigation, as needed.	This site condition is reported by investigators and regulators as the most common site condition associated with petroleum vapor intrusion sites.	<ul style="list-style-type: none"> <li>Impact to structure below depth of building foundation (e.g., dry well, elevator shaft)</li> <li>Intermittent vapor intrusion associated with high water-table events</li> </ul>
Dissolved source (benzene > 1000 ug/L, TPH>10,000 ug/L) with less than 5 feet vertical separation between source and building	Medium	Site-specific evaluation of bioattenuation in vadose zone (e.g., API 2005) and building evaluation, if needed.	<ul style="list-style-type: none"> <li>Modeling studies indicate that effectiveness of bioattenuation will be site-specific (API 2009)</li> <li>Many examples in published literature with high bio-attenuation and no vapor intrusion for this site condition (e.g., Ostendorf and Kampbell, 1991)</li> <li>A review of available field data found &gt;100x attenuation of benzene vapors in the vadose zone for &gt;95% of measurement events (Davis 2006)</li> <li>VI reported at a few sites with shallow NAPL sources (e.g., Sanders &amp; Hers, 2006)</li> </ul>	<ul style="list-style-type: none"> <li>Poor site characterization fails to identify shallower LNAPL sources</li> <li>Vapor intrusion associated only with some specific petroleum hydrocarbons (e.g., Sanders and Hers 2006)</li> <li>Intermittent vapor intrusion</li> <li>Preferential pathways</li> </ul>
LNAPL source with greater than 10 m (30 ft) separation between source and building.	Minimal	No need to assess the VI pathway	<ul style="list-style-type: none"> <li>No published examples of petroleum vapor intrusion for this site condition.</li> <li>Modeling studies indicate bioattenuation will limit the potential for vapor intrusion (API 2009; DeVaul 2007)</li> </ul>	<ul style="list-style-type: none"> <li>Poor site characterization fails to identify shallower LNAPL source</li> <li>Preferential pathways</li> </ul>
Dissolved petroleum hydrocarbons (i.e., benzene <1 mg/L and TPH <10 mg/L) in groundwater and greater than 5 feet separation between source and building.	Minimal	No need to assess the VI pathway	<ul style="list-style-type: none"> <li>No published examples of petroleum vapor intrusion for this site condition, in contrast to similar chlorinated VOC sites.</li> <li>Modeling studies indicate bioattenuation will limit the potential for vapor intrusion (API 2009; DeVaul 2007)</li> <li>Even low O<sub>2</sub> flux into subsurface can meet low O<sub>2</sub> demand from source</li> </ul>	<ul style="list-style-type: none"> <li>Poor site characterization fails to identify un-weathered residual LNAPL source</li> <li>Rise in water table brings contamination in contact with foundation</li> <li>Preferential pathways</li> </ul>

## Additional Information Regarding Soil Vapor Sampling

Soil vapor sampling is discussed in the Site Assessment chapter of this Manual. The following discussion provides additional information.

Selection of a sampling method is dependent on the objectives of the study, the COCs, and the required sampling duration. The methodology should be able to detect compounds at ambient levels, generally in the parts per trillion (ppt) to parts per billion (ppb) range for environmental samples. The methodology should produce results which are accurate and reproducible with a minimum of contamination problems. Finally, the methodology should allow for sampling periods which are representative of occupants' exposure time (MADEP 2002).

Indoor air sampling has the following challenges:

- Access to homes for the collection of indoor air samples may be difficult and intrusive.
- Interpretation of analytical results is challenging due to interferences by background sources of the COCs.
- Many commonly used household products contain some of the target COCs.

### Ambient Outdoor Air Sampling

Outdoor air samples are typically recommended when indoor air sampling is conducted (DTSC 2005, ITRC 2007). The outdoor air samples will assist in the identification of potential ambient source contributions to indoor air analytical data. The same sampling methodology discussed in *Indoor Air Sampling* should be considered for outdoor air sampling.

### Additional Site Assessment Data

Supplemental data may be helpful for the VI pathway evaluation (API 2005; ITRC 2007; DTSC 2005). Supplemental data to consider collecting during site investigation include:

- 1) Soil physical property data. Boring logs and soil samples for physical property analysis (e.g., grain size analysis, soil porosity, volumetric moisture content) can be collected during the installation of the soil-vapor probes. These data will help refine the CSM and may be used for refined VI modeling.
- 2) Building data. An assessment of building construction (e.g., is a vapor barrier present, depth of building foundation, are sump pumps present) and heating, ventilation, and air conditioning (HVAC) design and operation may be used to refine the CSM and evaluate whether building factors may limit VI.
- 3) Surface flux measurements. Surface flux-chamber measurements may be used to evaluate the flux of VOCs to the surface and reduce the uncertainty associated with the diffusion of VOCs through soil.
- 4) Determination of Slab-Specific Attenuation Factor Using Tracers

Measurement of a conservative tracer inside the structure and in the sub-slab soil gas can allow a site-specific attenuation factor to be calculated. The calculated attenuation factor can then be used to estimate the indoor air concentration of other contaminants of concern by multiplying the measured sub-slab soil gas concentration by the attenuation factor for the tracer (or "marker compound"). This method assumes that all sub-slab vapor phase contaminants are entering the building at equal rates, a relatively safe assumption for most situations. Naturally occurring radon is the most commonly used conservative tracer. Other potential tracers include breakdown products such as 1,1-DCE or cis-1,2-dichloroethene, which are generally not found in consumer products, building materials or outdoor air. Complications to this technique include the presence of indoor sources of the tracer (if any) and any temporal variations. However, if sub-slab samples are being collected, concurrent collection of radon or another tracer data may prove useful and is generally not too expensive. Determination of radon concentration using adsorbents is possible for indoor air samples, but not for soil gas samples including sub-slab samples. Soil gas methods exist for the collection of sub-slab radon concentration measurements (USEPA 2006), but analysis of the samples may not be readily available from most commercial laboratories.

### Determination of Room Ventilation Rate Using Tracers

The indoor air concentration is inversely proportional to the room ventilation rate: a two-fold increase in ventilation rate decreases the indoor air concentration by two-fold. The default ventilation rates used by the USEPA and many other agencies are conservative: room exchange rates of once every 1 to 4 hours for residences and once every hour for commercial buildings. For some structures, typically commercial buildings, the actual ventilation rate can be determined from the HVAC system or building design specifications, keeping in mind that the air exchange rate should be calculated from the make-up volume, not the total air handling volume. For other structures, typically residences, this information is

not readily available so the ventilation rate must be either the default value or it must be measured. ASTM Method E 741 describes techniques for measuring ventilation rates using gaseous tracers such as helium or sulfur hexafluoride ( $\text{SF}_6$ ).

Typically, a pulse input of tracer gas is applied and the decay in concentration versus time is measured. The inverse of the air exchange rate is the slope of a plot of natural logarithm of the normalized concentration ( $C_{t=n}/C_{t=0}$ ) versus time. If a subsurface tracer gas is used, this can serve as the pulse input. Alternatively, a tracer gas can be released at a constant rate and the concentration measured once steady-state conditions are reached (i.e., typically after three or four air exchanges).

The techniques are quick and relatively inexpensive. For colder climates, measurement during the cold and warm seasons may be prudent if the ventilation rate during the more conservative case (cold season) suggests unacceptable indoor air concentrations.

### Differential Pressure Measurements

Models and look-up values used by the USEPA and many state regulatory agencies are based on assumed advective flow into the structure due to a pressure gradient of 4 Pa. This assumption can be checked in the field to provide another line of evidence to evaluate vapor intrusion using a digital micromanometer attached to a sub-slab soil gas probe. It is often advisable to use one with data-logging capabilities and assess the response to wind speed and barometric pressure changes if these data are collected.

Measurement of the pressure gradient between the structure and outdoors can assist in interpreting measured indoor concentrations of contaminants. A correlation between indoor air concentration and relative pressure could provide information on the contaminant source. For example, if a building is over-pressured relative to the sub-surface, measured indoor concentrations might be more likely attributed to above-ground sources. Conversely, if the building is under-pressured relative to the sub-surface, measured indoor concentrations might be more likely attributed to sub-surface sources. Commercial buildings with large HVAC systems, and perhaps residences with AC units, may fall into the former category. Many structures in cold environments, especially residences, will fall into the latter category when the heaters are running. This will usually be used as a secondary line of evidence in support of indoor air quality data or other lines of evidence.

### Real-time & Continuous Analyzers

As with any type of site investigation, it is difficult to reach any conclusions with any degree of confidence with only a handful of data points. Vapor intrusion data sets consisting of one soil gas and/or indoor air analysis per structure may be very difficult to interpret, but cost and access limitations often preclude multiple analyses. Real-time analyzers can be used to collect multiple, less expensive data that can be used to locate problem structures, vapor migration routes into structures, and VOC sources inside the structures. Continuous analyzers that collect data automatically over a period of time can sort out background scatter and determine temporal variations both indoor and below-ground. Larger data sets allow trends in the results to be recognized and correlated to other variables such as pressure differentials, wind speed, and HVAC systems. Larger data sets allow forensic approaches to be applied.

A variety of real-time analyzers exist including hand-held logging instruments (PID, FID, TCD, IR analyzers, zNose<sup>®</sup>, and ppbRAE), automated gas chromatographs, portable mass spectrometers, and the USEPA's own trace atmospheric gas analyzer (TAGA).

### Laboratory Analysis

The analytical methods selected for a VI investigation are dependent upon the regulatory requirements and DQOs for a given site. Fixed labs, mobile labs, or field monitoring equipment may be suitable for the purpose, provided that the method detection limits and quality assurance/quality control (QA/QC) are appropriate for the intended use of the analytical results.

The recommended target analytes and analytical methods for vapor samples are discussed in the Analytical Requirements Chapter. A more complete list of available methods can be found in ITRC 2007 and API 2005.

### Data Analysis

The following steps should be considered in the data-evaluation process (API 2005):

- **Data Organization:** The data should be tabulated and plots made to summarize the variation of the concentration measurements in space and time.

- **Data Analysis:** The data should be reviewed to assess whether they are consistent with the CSM and internally consistent (i.e., do trends for different constituents behave in a similar manner that is also consistent with the CSM). If the data are not consistent with the CSM, then either update/revise the CSM or verify the data quality. If the data are not internally consistent, then the analytical results may not meet the DQOs for the assessment.
- **Exposure Pathway Assessment:** The data should be reviewed to assess whether the VI pathway is complete. If the pathway is not considered complete, the specific part (e.g., contaminant source, transport mechanism, exposure point, route of exposure, and/or receptor population) should be identified and documentation/ justification provided for this conclusion.
- **Identification of Additional Action:** After the preceding steps are complete, potential additional actions should be assessed. These corrective-action needs may include additional site-characterization data collection, source remediation, implementation of institutional controls, or mitigation measures.

## Mitigation

This section gives a brief overview of mitigation options. A comprehensive treatment can be found in the ITRC vapor intrusion guidance (ITRC 2007).

Various different approaches to the mitigation of VI have been proposed and are in use. The DTSC has issued internal guidance on considerations for the implementation of VI mitigation measures for site corrective action programs (DTSC 2009). When site investigations and/or quantitative risk assessments yield results which indicate the presence of potentially significant health risks associated with the VI exposure pathway, mitigation measures and engineering controls may be used to mitigate both short- and long-term exposure.

### Sub-Surface Source Removal

Source removal efforts serve to reduce the potential for future generation of vapors capable of migrating toward the ground surface and indoor air. This mitigation technique targets the sources of VOC vapors beneath the ground, including those present as solids adsorbed to unsaturated soils, those dissolved in groundwater, or those remaining as NAPLs trapped in the subsurface. Common source-removal options include soil excavation and offsite disposal, in-situ chemical oxidation (ISCO), enhanced biodegradation techniques, groundwater extraction and treatment, soil-vapor extraction (SVE), and dual-phase (vapor and water) extraction (DPE).

### Engineering Controls

#### 1. HVAC Optimization

A common engineering control implemented as a short- to medium-term solution, or in cases where the potential for VI is considered marginal, is optimization of HVAC operation parameters. This involves modification of parameters such as ventilation rates, as outlined by the American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE): [www.ashrae.org/technology/page/548](http://www.ashrae.org/technology/page/548), in an effort to optimize dilution and improve indoor air quality. This approach must account for ambient outdoor air quality, which is the typical source of the “clean” air used to dilute the otherwise impacted indoor air quality.

#### 2. Vapor Barriers

In addition to and/or in lieu of residual source removal and HVAC optimization, other types of engineering controls typically target the creation of barriers to migration of vapors through cracks and openings in building foundations. For future buildings slated for construction over VOC plumes, vapor barriers reflect a widely used engineering control for restricting VI through building foundations. Typical vapor barriers include use of polyethylene liners, elevated sub-floors such as Cupolex<sup>®</sup>, composite liners such as Geo-Seal<sup>™</sup> and Liquid Boot<sup>®</sup>, often placed beneath the foundation of buildings prior to construction. In certain cases, liquid liners may be introduced on top of existing foundations to seal cracks and/or joints/openings. These barriers serve to fill in and/or cover potential conduits in building foundations, thereby eliminating the potential for migration of vapors to indoor air. Additional methods for creating vapor barriers include:

- Sealing cracks and penetrations
- Spray-on rubberized asphalt membranes
- Aerated floor systems (air-tight raised floor)

The key to barriers is the integrity of the seal; the barriers should survive construction foot traffic, dropped tools, rebar, and poured concrete. Integrity tests should be conducted (smoke tests, indoor air tests) to ensure the efficiency of the system.

### 3. Sub-Slab Depressurization Systems (SSDs)

Another category of engineering controls relates to SSDs, which serve a purpose similar to that of vapor barriers, but which achieve their objective by eliminating the pressure differential pulling vapors from the subsurface to indoor air. Specifically, properly designed SSDs serve to maintain a lower pressure beneath the building foundation in comparison to the pressure above the foundation and indoor air, thereby eliminating the pressure gradient governing VI. To achieve this goal, SSDs, which may be installed in existing and/or future buildings, are designed as either active or passive systems. The former utilizes an electric fan or blower, while the latter is vented directly to the atmosphere and may use a roof-mounted, non-powered fan. Active SSD systems typically consist of a fan or blower that draws air from the soil beneath a building, discharging it into the atmosphere through a series of collection and discharge pipes. Holes cut through the building foundation allow for placement of extraction pipes in contact with sub-surface materials, resulting in removal of soil vapor from beneath the building foundation. The exhaust from the blower is generally routed away from windows, doors, or other openings in the building using polyvinyl chloride pipe or rain gutter downspout material.

The above engineering control alternatives for mitigation of VI may be implemented independently or in combination with one another, and are typically supplemented by soil-vapor monitoring or indoor air monitoring to demonstrate the effectiveness of system operations and for protection of public health.

A range of factors should be evaluated in the selection of an appropriate mitigation system to address VI concerns (DTSC 2009):

- System effectiveness
- Long-term operation and maintenance requirements
- Permitting requirements
- Property owner impacts
- Public participation needs
- Enforcement requirements
- Financial assurance requirements

These factors may influence which technology is selected for VI mitigation at a particular site.

## References

- Abreu, L.D.V., R. Ettinger, and T. McAlary. 2009. Simulated Soil Vapor Intrusion Attenuation Factors Including Biodegradation for Petroleum Hydrocarbons. *Ground Water Monitoring & Remediation*, Vol. 29, No. 1: 105-117.
- Abreu, L.D.V., and P.C. Johnson. 2006. Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into Buildings: Influence of Degradation Rate, Source Concentration, and Depth. *Environ. Sci. Technol.* Vol. 40, No. 7: 2304-15.
- American Petroleum Institute (API). 2001. Vadose Zone Natural Attenuation of Hydrocarbon Vapors: An Empirical Assessment of Soil Gas Vertical Profile Data. API Soil and Groundwater Task Force Bulletin Number 15. December.
- API. 2005. Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites. API Publication Number 4741. November.
- API. 2009. Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into Buildings, Evaluation of Low Strength Sources Associated with Dissolved Gasoline Plumes. API Publication 4775. April.
- American Society for Testing and Materials (ASTM). 2008. [ASTM E2600 - 08 Standard Practice for Assessment of Vapor Intrusion into Structures on Property Involved in Real Estate Transactions](#).
- California Department of Toxic Substances Control (DTSC). 2005. Interim Final Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air. December 15, 2004, Revised February 7, 2005.
- DTSC. 2009. Vapor Intrusion Mitigation Advisory, Department of Toxic Substances Control, California Environmental Protection Agency. April.
- Davis, Robin V. 2006. Vapor Attenuation in the Subsurface from Petroleum Hydrocarbon Sources. *LUSTLine Bulletin*, 52 (May 2006): 22-25.



- Davis, Robin V. 2009. Update on Recent Studies and Proposed Screening Criteria for the Vapor Intrusion Pathway. LUSTLine Bulletin, 61 (May 2009), pp. 11-15. Available at [http://www.neiwpcc.org/lustline/lustline\\_pdf/lustline\\_61.pdf](http://www.neiwpcc.org/lustline/lustline_pdf/lustline_61.pdf) Accessed on 1/22/10
- Davis, G.B., B.M. Patterson, and M.G. Treffry. 2009. Evidence for instantaneous oxygen-limited bio-degradation of petroleum hydrocarbon vapors in the subsurface. Ground Water Monitoring & Remediation Vol. 29, No. 1: 126-137.
- DeVaul, G. E. 2007. Indoor Vapor Intrusion with Oxygen-Limited Biodegradation for a Subsurface Gasoline Source. Environ. Sci. Technol. Vol. 41: 3241-48.
- Fischer, M.L., A.J. Bentley, K.A. Dunkin, A.T. Hodgson, W.W. Nazaroff, R.G. Sextro, and J.M. Daisey. 1996. Factors Affecting Indoor Air Concentrations of Volatile Organic Compounds at a Site of Subsurface Gasoline Contamination. Environ. Sci. Technol. Vol. 30, No. 10: 2948-57.
- Interstate Technology and Regulatory Council (ITRC). 2007. Vapor Intrusion Pathway: A Practical Guide. January.
- Los Angeles Regional Water Quality Control Board (LARWQCB)/DTSC. 2003. Advisory – Active Soil Gas Investigations. January 28.
- Lundegard P.D. and P.C. Johnson. 2006. Source Zone Natural Attenuation at Petroleum Hydrocarbon Spill Sites II: Application to a Former Oil Field. Ground Water Monitoring & Remediation, Vol. 26, No. 4: 93-106.
- Lundegard, P.D., P.C. Johnson, and P. Dahlen. 2008. Oxygen transport from the atmosphere to soil gas beneath a slab-on-grade foundation overlying petroleum-impacted soil. Environ. Sci. Technol. Vol. 42, No. 15: 5534-40.
- Luo, H., P. Dahlen, P. C. Johnson, T. Peargin, and T. Creamer. 2009. Spatial variability of soil-gas concentrations near and beneath a building overlying shallow petroleum hydrocarbon-impacted soils. Ground Water Monitoring & Remediation, Vol. 29, No. 1: 81-91.
- Massachusetts Department of Environmental Protection [MADEP]. 2002. Indoor Air Sampling and Evaluation Guide. April.
- McHugh, T.E., P.C. DeBlanc, and R.J. Pokluda. 2006. Indoor air as a source of voc contamination in shallow soils below buildings. Soil and Sediment Contamination. Vol. 15: 103-122.
- Newell, C.J., and J.A. Connor. 1998. Characteristics of Dissolved Petroleum Hydrocarbon Plumes, Results from Four Studies. API, Washington, D.C.
- New York State Department of Health [NYSDOH]. 2005. Indoor Air Sampling and Analysis Guidance. February 1.
- Ostendorf, D. W., and D. H. Kampbell. 1991. Biodegradation of hydrocarbon vapors in the unsaturated zone. Water Resources Research. Vol. 27: 453-462.
- Parker, J.C. 2003. Modeling volatile chemical transport, bio-decay, and emission to indoor air. Ground Water Monitoring & Remediation, Vol. 23, No. 1: 107-120.
- Pasteris, G., D. Werner, K. Kaufmann, and P. Hohener. 2002. Vapor Phase Transport and Biodegradation of Volatile Fuel Compounds in the Unsaturated Zone: A Large-Scale Lysimeter Experiment. Environ. Sci. Technol. Vol. 36, No. 1: 30-39.
- Regional Water Quality Control Board (RWQCB) - North Coast. 2009. Vapor Intrusion Guidance Document. July.
- Sanders, P.F. and I. Hers. 2006. Vapor intrusion in homes over gasoline-contaminated ground water in Stafford, New Jersey. [Ground Water Monitoring & Remediation](#), Vol. 26, No. 1: 63-72.
- Turk, B., R. Prill, D.T. Grimsurd, B.A. Moed, R.G. Sextro. 1990. Characterizing the occurrence, sources, and variability of radon in Pacific Northwest homes. Journal of the Air Waste Management Association. Vol. 40, No. 4: 498-506.
- United States Environmental Protection Agency (USEPA). 2002. Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). Office of Solid Waste and Emergency Response, USEPA Publication No. EPA530-D-02-004. November.
- USEPA. 2006. Assessment of Vapor Intrusion in Homes Near the Raymark Superfund Site Using Basement and Sub-Slab Air Samples. Office of Research and Development, National Risk Management Research Laboratory, Ground Water and Ecosystems Restoration Division, USEPA Publication No. EPA/600/R-05/147. March.